VOL. XLIX FEBRUARY, 1913 NO. 2

AMERICAN

CHEMICAL JOURNAL

ON THE NITRILE OF FUMARIC ACID AND THE PREPARATION OF METHYL MALEATE

BY EDWARD H. KEISER AND L. MCMASTER

In the synthesis of fumaric and maleic acids from acetylene by means of the iodides and potassium cyanide the nitriles of the acids were not isolated. Subsequently E. H. Keiser and J. J. Kessler[1] obtained the nitrile of fumaric acid by heating fumaramide with phosphorus pentoxide. The long, slender needles that formed as a sublimate undoubtedly had the composition of fumaric nitrile. They had a pleasant odor and when treated with alkalis gave off ammonia. In short, the behavior of the substance was such as one would expect from a cyanide. Difficulty was experienced, however, in trying to convert the fumaric nitrile into fumaric acid. This was no doubt due to the fact that the quantities worked with were small. We have now prepared the nitrile in larger quantities and have succeeded in converting it back into fumaramide and into fumaric acid, thus establishing, beyond all doubt, its constitution.

This conversion was found to take place readily by means of an alkaline solution of hydrogen dioxide,[2] the action taking place according to the equation:

[1] THIS JOURNAL, **46**, 523.
[2] Ber. d. chem. Ges., **18**, 355.

$$\begin{matrix} CHCN \\ \| \\ CHCN \end{matrix} + 2H_2O_2 = \begin{matrix} CHCONH_2 \\ \| \\ CHCONH_2 \end{matrix} + O_2$$

The fumaramide thus formed was then transformed into fumaric acid by warming with dilute caustic potash.

Twenty-five hundredths gram of fumaric nitrile was treated with 25 cc. of a 3 per cent. solution of hydrogen dioxide and the liquid made faintly alkaline with a few drops of caustic soda solution. There was a rapid evolution of oxygen and after a short time a white precipitate separated. This was removed by filtration, and was found to be insoluble in cold water, in alcohol and ether, but was soluble in hot water, thus showing the properties of fumaramide. In determining the melting point, it became black at 232° and melted completely at 267°. For the sake of comparison a sample of fumaramide was prepared from diethyl fumarate by the action of ammonia and this behaved in the same way as that obtained from the nitrile. The melting point of fumaramide is given by Curtius and Koch[1] at 232° "with carbonization." Hell and Poliakow[2] give it at about 266°. With a second specimen of the fumaramide made from the nitrile we found that at 233° the substance became black and at 267° it melted sharply.

The fumaramide thus made from fumaric nitrile was then hydrolyzed by warming upon the water bath for one hour with dilute caustic potash. All odor of ammonia was then gone and the solution was allowed to cool and was then neutralized with dilute nitric acid. Silver nitrate was added and a white precipitate of silver fumarate was formed. This was filtered, washed and dissolved in dilute ammonia and reprecipitated by again neutralizing with nitric acid. The precipitate, after filtering and washing, was dried at 100°. On analysis the following result was obtained:

0.0628 gram substance gave 0.0543 gram AgCl.

	Calculated for $C_3H_2O_4Ag_2$	Found
Ag	65.4	65.1

[1] J. prakt. Chem., [2] **38**, 478.
[2] Ber. d. chem. Ges., **25**, 643.

The dried salt deflagrated like gunpowder when heated, this being one of the characteristic properties of silver fumarate. It was also insoluble in boiling water, a fact which distinguishes it from silver maleate.

Another portion of fumaramide made from the fumaric nitrile by means of hydrogen dioxide was saponified by alcoholic potash. As the amide is only slightly soluble in absolute alcohol, the solution was boiled for 16 hours. It was then filtered and evaporated to remove the alcohol, water added, and the alkali neutralized with nitric acid. The silver salt was then precipitated, washed, dried and analyzed.

0.1016 gram substance gave 0.0877 gram AgCl.

	Calculated for $C_4H_2O_4Ag_2$	Found
Ag	65.4	65.0

Dimethyl Maleate.—This ester has heretofore been made by the action of methyl iodide upon silver maleate. We have succeeded in preparing it from methyl alcohol, maleic acid and sulphuric acid. Five grams of maleic acid, 50 cc. of methyl alcohol and 2 cc. of concentrated sulphuric acid were boiled for four hours under an inverted condenser. The liquid was then poured into an evaporating dish and the alcohol allowed to evaporate. The residue was stirred up with barium carbonate and allowed to stand in contact with it for several days. Ether was added to the mixture and the solid matter separated by filtration. The ether was removed from the filtrate by evaporation and the thick oily residue, consisting of dimethyl maleate, was distilled. Its boiling point was found to be 203°. A small quantity of a solid melting at 102° was found in the condenser; this was dimethyl fumarate. That the clear distillate was dimethyl maleate was proved by adding bromine water to a portion of it. On standing, a white solid crystalline compound was obtained. This was recrystallized from its solution in ether. It melted at 102° and had all of the properties of dimethyl fumarate.

We have also studied the action of ammonia upon dimethyl maleate. When a mixture of the ester and ammonia solution was allowed to stand several days, the oil gradually dissolved

but no precipitate of amide was formed as in the case of the dimethyl fumarate. On evaporating slowly, after the ammonia and water were removed, a thick yellowish oil remained, which became semisolid when it was stirred and was very difficult to detach from the platinum dish in which it was contained. A portion of it, when heated, acquired a red color. Another portion, when mixed with phosphorus pentoxide, gradually became hot and as the mass turned black a white sublimate came off which was condensed in an inverted funnel. This sublimate melted at from 135° to 138,° and may have been the nitrile of maleic acid. A third portion was warmed with caustic soda and ammonia was given off. In all probability this thick gluelike mass was the amide of maleic acid.

A GENERAL METHOD FOR THE PREPARATION OF THE AMMONIUM SALTS OF ORGANIC ACIDS

By Edward H. Keiser and L. McMaster

The usual method of preparing the ammonium salts of organic acids, namely, neutralizing the aqueous solution of the acid with ammonia and evaporating to crystallization, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts. A study of the literature of ammonium salts of organic acids shows that comparatively few of them have been made and analyzed. In the case of dibasic acids usually only the acid ammonium salt has been prepared.

In attempting to prepare the amide of maleic acid we desired to start with the diammonium maleate, but found it impossible to make this salt by neutralizing a solution of maleic acid with ammonia and evaporating to crystallization. We, therefore, dissolved the acid in ether and conducted a stream of dry ammonia gas into the ethereal solution. A white, flocculent, rather gelatinous precipitate at first formed, this soon collected into lumps and, on continuing to pass in ammonia, changed into a white crystalline powder. Analysis showed it to be diammonium maleate.

This method of preparing diammonium maleate was found

to be applicable in a general way to the preparation of the ammonium salts of other organic acids. In those cases in which the acid was insoluble in ether some other solvent, such as absolute alcohol, or a mixture of ether and alcohol, was used. The method is dependent upon the fact that most organic acids are soluble in ether or alcohol or a mixture of the two, while the ammonium salts are insoluble and can be thrown down by means of a stream of dry ammonia gas. Very good yields are obtained by this method. The organic salts of other weak bases, such as the salts of aniline, the amines and other organic bases can, no doubt, be made in the same general way by doing away with aqueous solutions and using only alcoholic or ethereal solutions of both acid and base.

We have made, in this way, the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic and phthalic acids.

Ammonium Maleate.—This salt was precipitated from the ethereal solution of the acid by a stream of dry ammonia, as described above, washed on the filter with ether and dried in the air. It is a white, crystalline powder, not deliquescent in the air but readily soluble in water. Büchner[1] describes this salt as being deliquescent, but his compound was prepared in the wet way. This salt has an odor similar to that of acetamide.

Analyses gave the following results:

	Calculated for $C_2H_2(CO_2NH_4)_2$	Found			
		I	II	III	IV
C	31.97	...	31.20	32.04	32.06
H	6.71	...	7.09	6.89	6.91
N	18.66	16.12	16.13	18.70	18.46

The first two nitrogen determinations were made by the Kjeldahl method and gave low results, the last two by the Dumas method. We also prepared this salt by precipitation with ammonia in a solution of the acid in absolute alcohol.

Ammonium Fumarate.—Fumaric acid was dissolved in absolute alcohol and dry ammonia conducted into the solution. A heavy white amorphous powder was at once formed. It was filtered, washed thoroughly with alcohol and ether and

[1] Büchner: Ann. Chem. (Liebig), **49**, 67.

dried in air, on a porous plate. This salt has no odor, as in the case of the diammonium maleate. It is not deliquescent but dissolves readily in water. It gave, on analysis, the following results:

	Calculated for $C_2H_2(CO_2NH_4)_2$	Found I	Found II
N	18.66	18.47	18.50

Ammonium Mesaconate.—The mesaconic acid, obtained from Kahlbaum, was dissolved in ether and dry ammonia conducted into the solution. A gelatinous precipitate was at first formed but this soon changed into a crystalline powder. The salt was filtered, washed on the filter with ether and then dried in the air. Like the ammonium fumarate, it had no odor. It was not deliquescent but dissolved readily in water. Determinations of nitrogen gave the following results:

	Calculated for $CH_3C_2H(CO_2NH_4)_2$	Found I	Found II
N	17.07	16.71	16.84

Ammonium Citraconate.—Citraconic acid (Kahlbaum) was dissolved in ether and ammonia passed into the solution. A thick colloidal solution was at first formed, but as the ammonia continued to pass into the solution this changed into a crystalline precipitate. This was filtered, washed with ether and dried in the air. Like the ammonium maleate it has an odor like that of acetamide. The salt is not deliquescent but soluble in water.

	Calculated for $CH_3C_2H(CO_2NH_4)_2$	Found I	Found II
N	17.07	16.82	16.87

The ammonium salts of malonic and phthalic acids were also made by the same general method. The ammonium malonate came down in ether solution as a fine white crystalline precipitate. It had no odor and was not deliquescent, although readily soluble in water. The ammonium phthalate was obtained as a white powder.

[Contribution from the Chemical Laboratories of Columbia University, No. 213]

A QUANTITATIVE STUDY OF SOME ALDEHYDE REACTIONS[1]

By B. G. Feinberg

INTRODUCTION

The great and constantly growing commercial importance of aldehydes makes definite methods of analysis of great value. It is, therefore, not surprising to note that the literature on the subject is quite extensive. Although a considerable amount of work has been carried out in comparing certain of the methods with a view to determining the most acccurate, it is worthy of note that little has been done to determine the general applicability of methods, nor has a systematic quantitative study of the behavior of certain typical aldehydes towards various reagents been undertaken.

On account of the reactivity of the carbonyl group, aldehydes are capable of taking part in many reactions. Those which, in addition to the aldehyde group, also have other characteristic groups will, in turn, take part in special reactions peculiar to those groups.

Methods may therefore be classified as general when the characteristic reactions of the aldehyde group alone are considered, and special when the properties of any of the other groups present are taken advantage of for purposes of analysis.

Among the general methods (*a*) the combination of aldehydes with bisulphite, (*b*) the reaction with neutral sulphite, and (*c*) the precipitation of aldehydes as hydrazones were selected for special study.

Purpose and Plan

This work was therefore undertaken:

1. To note how nearly quantitative the general methods mentioned above were with the following typical aldehydes: formaldehyde, benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisic aldehyde and vanillin.

[1] A part of this paper was read before the section on Analytical Chemistry of the Eighth International Congress of Applied Chemistry, Washington and New York, Sept. 4–13, 1912.

2. Wherever possible, to establish conditions that would permit of the accurate determination of an aldehyde by a given method.

3. To study the effect upon the different methods of determination of such factors as the increasing molecular weight and the presence of various groups in addition to the aldehyde group.

The purest material possible was procured, its purity ascertained by the application of well known tests, by redistillation at reduced pressure, recrystallization or sublimation. Also, wherever possible, the best tested or approved special methods were used as checks.

Wherever the results obtained, on applying a method to a pure aldehyde, did not approximate the theoretical, the conditions of the determinations were varied until those giving the best results were obtained, or the method proven to be inapplicable on account of the nature of the product or the incompleteness of the reaction.

This work was undertaken at the suggestion of Professor H. C. Sherman, and was carried out under his direction partly at Columbia University and partly at the College of the City of New York, through the courtesy of the Director of the Laboratory.

THE BISULPHITE METHOD

Bertagnini,[1] in 1853, established the fact that bisulphite combined with substances of aldehydic nature. In 1890[2] this was introduced by Schimmel and Company, for the determination of cinnamic aldehyde in cassia oil. It now plays an important part in the valuation of oils containing citral and cinnamic aldehyde. The method of determination consists in treating a known volume of oil with sodium bisulphite in a cassia flask, shaking well and allowing to stand for some time. The oil is then brought up to the graduated portion of the flask, and the volume of uncombined oil is read off. The aldehyde present is thus determined by difference.

In 1901, M. Ripper[3] suggested using a dilute bisulphite solu-

[1] Semmler: Die aetherischen Oele, **1**, 156.
[2] Gildemeister and Hoffmann: Die aetherischen Oele, 2nd Ed., p. 602.
[3] Monats. Chem., **21**, 1079.

tion with dilute aldehyde solutions, and determining the excess of bisulphite with a standard iodine solution. Ripper uses potassium bisulphite and claims good results with formaldehyde, acetaldehyde, benzaldehyde and vanillin.

The method, as applied here, was essentially that of Ripper with the exception that solutions of various concentrations were employed.

The purification of material and the conditions which gave the best results are described below.

Formaldehyde.—The formaldehyde used was Kahlbaum's pure product, which had previously shown 33.76 per cent. aldehyde by the Blank and Finkenbeiner peroxide method.[1]

Previous investigation in the Columbia laboratory[2] had shown the Romijin[3] iodine method to be admirably adapted to the determination of formaldehyde in relatively pure solutions. This method was, therefore, chosen as another means of determining the formaldehyde content of the sample used in the investigation. The author, however, slightly modified the Romijin conditions so as to use twice the amount originally suggested. The error in measuring a small amount of solution is thus decreased, and more consistent results were obtained.

The conditions as used are therefore as follows: Ten cc. of a solution of formaldehyde of about 0.5 per cent. strength were treated in a stoppered Erlenmeyer flask with forty cc. of a standard iodine solution, about tenth normal, made up with thirty-five grams potassium iodide per liter, ten cc. normal sodium hydroxide added, and allowed to stand fifteen minutes; ten cc. normal sulphuric acid were then added and the excess of iodine determined with about tenth normal thiosulphate. By means of a blank, the amount of iodine used up by the aldehyde present is ascertained, and from the factor—one gram iodine equivalent to 0.11858 gram formaldehyde—the aldehyde equivalent of one cc. of iodine solution can be obtained. The average of fourteen determinations by this method showed 33.86 per cent. aldehyde.

[1] Ber. d. chem. Ges., **31,** 2979.
[2] Williams: J. Am. Chem. Soc., **27,** 596.
[3] Z. anal. Chem., **36,** 18.

Solutions of sodium bisulphite were now used upon an aldehyde solution of the above mentioned concentration. A three per cent. bisulphite solution gave results which approached the closest to those obtained above with the Romijin method. The figures in Table I were obtained by treating 25 cc. aldehyde solution of about 0.5 per cent. strength with 25 cc. of 3 per cent. bisulphite solution, in a stoppered Erlenmeyer flask. After standing about fifteen minutes, during which a blank is run, the excess of bisulphite is titrated with tenth normal iodine and the per cent. of aldehyde calculated from the iodine equivalent of the formaldehyde, mentioned above.

Benzaldehyde.—For use with bisulphite a high grade of commercial benzaldehyde was first distilled at the ordinary pressure and that fraction which came over at 178°.5–179°.0, corrected, using a standardized thermometer, was collected and redistilled in vacuum. At 110 mm. the boiling point of the aldehyde was found to be 112°.5, corrected. The main portion was then fractionated in vacuum, and that part which distilled over at 112°.5–113° at 110 mm. was caught in an amber-colored bottle and tightly stoppered at once. Oxidation was therefore reduced to a minimum.

A one per cent. aldehyde solution in 100 cc. of 95 per cent. alcohol and 400 cc. water was prepared, and varying amounts of this solution were treated with different quantities of sodium bisulphite solutions, ranging in concentration from 1 to 6 per cent. and the excess determined with standard iodine. Results above 95 per cent., however, were not obtained. The aldehyde bisulphite compound is apparently hydrolyzed[1] very easily, for, in all cases, when the reaction mixture was titrated with iodine the end point could not be made to persist for more than an instant. If the titration were continued until a permanent end point was obtained, the amount of iodine used would almost be equal to that required by the bisulphite used alone. Attempts to render the reaction more nearly quantitative did not prove very successful. The addition of neutral sodium sulphite to diminish ionization of the acid formed during the titration appeared to give better re-

[1] W. Kerp: Z. Unters. Nahr. Genussm., **6**, 66; also Centralb., **1904**, II, 57.

sults, but still they were only about 95 per cent. of the theoretical.

The figures in the table were obtained by treating 25 cc. of the 1 per cent. aldehyde with 25 cc. of a 3 per cent. sodium bisulphite and allowing the mixture to stand about 25 minutes in a stoppered Erlenmeyer flask before titrating the excess of bisulfite.

Salicylaldehyde.—Salicylaldehyde was purified by fractionation under reduced pressure and only that which distilled at 139°–139°.5 at 160 mm. or 166°–166°.5 at 360 mm. was treated similarly to benzaldehyde. The results obtained were only about 82 per cent. of the theoretical, indicating that this aldehyde bisulphite compound was much less stable than the corresponding benzaldehyde compound. In order to ascertain whether the greater instability of the addition compound was due to the proximity of the acid hydroxyl group, experiments were conducted with *p*-hydroxybenzaldehyde and anisic aldehyde under conditions similar to those used for benzaldehyde.

p - *Hydroxybenzaldehyde.* — Kahlbaum's *p* - hydroxybenz - aldehyde was purified by sublimation and the fine, snow-white, needlelike crystals were found to have a melting point of 115°–116°. These were then used for the various determinations. With bisulphite the results were mainly 87–89 per cent. of the theoretical, thus showing that while the hydrolysis of the aldehyde bisulphite compound was greater in this case than for benzaldehyde,[1] it was considerably smaller than for salicylaldehyde. The presence and proximity of the hydroxyl group apparently influence the stability of the bisulphite addition compound.

Anisic Aldehyde.—On account of the relation between anisic aldehyde and vanillin on one hand, and benzaldehyde on the other, it was considered very interesting to determine how the former would behave in the various determinations.

Anisic aldehyde was therefore purified by repeated fractionation under reduced pressure and that which distilled at 195°–195°.5, corrected, at 205 mm. pressure, was used in the

[1] See Table I.

determinations. The results with bisulphite showed only about 90 per cent. of the theoretical amount present. This would indicate that, while the anisic aldehyde bisulphite compound was more easily hydrolyzed than that of benzaldehyde, it was not as readily hydrolyzed as the corresponding *p*-hydroxybenzaldehyde compound, and still less so than that of salicylaldehyde.

Vanillin.—Vanillin was specially purified by Isakovics by recrystallizing once from 50 per cent. ethyl alcohol, twice from 99 per cent. methyl alcohol, and once from absolutely anhydrous methyl alcohol. In order to remove vanillic acid, which was always formed when the vanillin was exposed to the air, he treated the material before the last crystallization with 1 per cent. sodium hydroxide solution sufficient to remove not only all the vanillic acid present, but also 5 per cent. of the vanillin, so as to be sure that all the acid had been taken out. He claimed that this treatment would give a vanillin about as pure as it could be made.

The vanillin prepared above, as well as materials prepared by Kahlbaum and by Fritzsche Bros., were used in the determinations.

When the conditions with bisulphite used heretofore were applied to the determination of vanillin the results of repeated determinations on the three preparations ranged from 93 to 96 per cent. of the theoretical. Attempts to make the reaction more nearly quantitative by increasing the concentration of the bisulphite, using potassium instead of sodium bisulphite or alcohol instead of water as a solvent for the vanillin, did not very materially change the figures. The vanillin-bisulphite addition product apparently is hydrolyzed to a smaller extent than any of the others tried, excepting formaldehyde.

The figures in the table were obtained by treating an approximately 1 per cent. aldehyde solution with 10–25 cc. of 3 per cent. sodium bisulphite solution in a stoppered Erlenmeyer flask and titrating after 15–25 minutes with a standard iodine solution until the blue color with starch persisted for an instant. The difference between the amount of iodine re-

Table I.—Bisulphite Results for the Different Aldehydes in Per Cent. of the Theoretical

Formaldehyde[1]	Benzaldehyde	Salicylaldehyde	*p*-Hydroxybenzaldehyde	Anisic aldehyde	Vanillin
98.70	93.45	80.48	88.40	89.90	A material
98.70	92.79	81.58	88.86	90.40	95.19
98.11	93.34	82.01	88.40	90.17	95.59
98.46	92.02	82.23	89.10		95.21
98.64	93.12	82.23	89.10		95.77
98.02	93.55		85.66		95.21
98.37	93.12		85.38		95.64
98.08	94.98		85.50		95.20
98.52	95.19		87.09		94.98
98.96	94.77		86.77		B material
98.70	92.89		87.09		94.50
99.11	93.71				94.40
99.44	93.61				94.50
98.79	94.03				94.63
99.44	93.82				94.31
Av. 98.67					94.18
					C material
					95.75
					95.75
					95.35
					95.72
					95.50

quired by a blank carried out under similar conditions and that required in the determination, gave the iodine equivalent to the amount of aldehyde used. The per cent. was calculated by using the factors obtained from the amount of aldehyde equivalent to 1 gram iodine, thus: 1 gram iodine is equivalent to 0.1186 gram formaldehyde, 0.4118 gram benzaldehyde, 0.4808 gram salicylaldehyde or *p*-hydroxybenzaldehyde, 0.5360 gram anisic aldehyde, 0.5990 gram vanillin.

W. Kerp[2] finds that the sodium bisulfite addition compounds of aldehydes and ketones are dissociated into their components in water. This is increased by a rise in temperature and lowered by an increase in concentration. He finds that the

[1] These figures were obtained by dividing the results by 33.86, the average result obtained with the Romijin method. This was done in order to make the results comparable with those in the other columns.

[2] Z. Unters. Nahr. Genussm., **6**, 66; also Centralb., **1904**, II, 57.

formaldehyde compound is most stable and gives the least bisulphite in solution; acetaldehyde gives five times as much bisulphite as the formaldehyde compound under the same conditions; benzaldehyde, thirty-one times as much; acetone, 155 times; and glucose, 500–1200 times as much as the formaldehyde compound. Titrating with iodine destroys the equilibrium between the undissociated addition compound, aldehyde and bisulphite, causing more bisulphite to form. A study of Table I will give an idea of the relative ease with which the addition compounds are probably dissociated.

Another cause for low results, though of less importance than that caused by the dissociation described above, would be the error in reading the burette. Thus, if that error be placed at about 0.01 cc. for a concentrated bisulphite solution, this would amount to about 0.1 cc. of iodine solution, which alone is sufficient to cause an error of three- to four-tenths of a per cent. on the amount of vanillin taken for an analysis.

Effect of Varying Conditions

Varying Excess of Reagent.—The effect of excess of reagent in different amounts as measured by the volume of iodine solution required to titrate the excess is shown in Tables II and III. In the first column the amount of bisulphite in excess required only about 5 to 15 cc. tenth normal iodine. In the second column a medium excess of bisulphite is used, requiring up to about 50 cc. tenth normal iodine. In the third the reagent is in still greater excess:

Table II.—Comparison of Results with Various Concentrations of Sodium Bisulphite on Formaldehyde

Excess equivalent to 5–15 cc. 0.1 N I Per cent.	Medium excess 25–50 cc. I Per cent.	Excess equivalent to about 50–75 cc. I Per cent.
96.69	99.11	97.66
97.16	99.44	98.14
95.89	98.52	
95.98	99.44	Av. 97.75
95.98	98.96	
95.98	98.70	
	98.37	
Av. 96.36	98.20	
	98.02	
	Av. 98.75	

Here the best results were obtained with an excess of bisulphite equivalent to 25–50 cc. iodine. A similar result was observed with benzaldehyde, as will be seen from Table III, which follows:

Table III.—Comparison of Results with Various Concentrations of Sodium Bisulphite on Benzaldehyde

Excess equivalent to 5–15 cc. 0.1 N I Per cent.	Medium excess 25–50 cc. I Per cent.	Excess equivalent to about 50–75 cc. I Per cent.
90.95	93.34	93.80
90.95	93.12	93.94
90.75	93.55	93.60
89.46	93.12	91.73
89.46	94.98	92.00
	95.19	92.84
Av. 90.31	94.77	92.20
	93.71	92.84
	93.61	92.62
	94.03	93.27
	93.82	92.41
	93.73	
	93.82	Av. 92.84
	Av. 93.90	

On vanillin the results obtained on decreasing the quantity of water by using alcohol as a solvent, or on substituting potassium bisulphite for the sodium compound, as well as on varying the concentration of bisulphite, are tabulated in Tables IV and V:

Table IV

0.10–0.15 gram vanillin in 50 cc. water Per cent.	0.1500–0.2000 gram vanillin in 5 cc. alcohol and 10 cc. water Per cent.
90.13	94.82
90.46	93.54
89.00	93.90
90.60	93.75
87.07	93.20
91.64	95.11
Av. 89.82	Av. 94.05

In Table V the effect of varying the concentration of sodium

bisulphite or employing potassium bisulphite on 25 cc. of a water solution of aldehyde containing 0.2000 to 0.2500 gram vanillin is tabulated:

Table V

Excess sodium bisulphite equivalent to 25–50 cc. I Per cent.	Excess equal to 50–75 cc. I Per cent.	Excess equal to about 100 cc. I Per cent.	Potassium bisulphite excess equal to about 25 cc. I Per cent.
95.40	96.37	88.64	94.75
95.70	95.72	88.72	94.63
95.40	95.72	88.06	94.82
95.70	95.59	87.40	94.63
93.22	95.21	89.05	94.50
93.22	95.77		94.40
95.00	95.21	Av. 88.39	
94.50			Av. 94.62
95.00	Av. 95.65		
94.40			
94.51			
94.82			
Av. 94.71			

It may be seen from Tables II, III and V that if the bisulphite is not in sufficient excess, the results are lower than when a considerable excess of reagent is present. If, on the other hand, the excess is still further increased, a point is reached where, because of the difficulty of handling bisulphite solutions of greater concentration and because of the decreasing stability of the aldehyde bisulphite compound (due to increasing acidity of the mixture), irregular and often much lower results are obtained. The amount of bisulphite in excess which gives the most favorable results may then be set as the one which requires about 50 cc. of tenth normal iodine to titrate in a volume of about 50 cc. The most convenient strength for this purpose is a solution of 2–3 per cent. sodium bisulphite and 25 cc. of such a solution can be handled without great error.

It may further be noted from Table V that potassium bisulphite is of the same efficiency as the sodium compound.

R. H. Williams,[1] working in this laboratory, compared the

[1] J. Am. Chem. Soc., **27**, 596.

Legler[1] ammonia method, the Blank and Finkenbeiner[2] peroxide oxidation method, the Romijin[3] iodine and potassium cyanide methods on formaldehyde. He found that the condensation methods give lower results than the oxidation methods, either because the oxidation goes further than the equation would indicate or more probably because the condensation is not quite complete. The results here obtained with the bisulphite method in the case of formaldehyde are in harmony with the conclusion reached by Williams.

THE NEUTRAL SULPHITE METHOD

According to some investigators, when neutral sodium sulphite in water solution acts on an aldehyde or ketone, sodium hydroxide is liberated thus:

$$R.CHO + Na_2SO_3 + H_2O = R.C(OH)NaHSO_3 + NaOH$$

The use of this reaction for the quantitative determination of aldehydes was first suggested by Tiemann.[4] Later Sadtler[5] stated that this reaction was more or less general for the quantitative determination of some saturated and unsaturated aliphatic and aromatic aldehydes, and some ketones. The method as worked out by him consists in titrating the alkali with normal acid. From the equation the amount of aldehyde present could be calculated.

A 20 per cent. sodium sulphite solution was prepared and neutralized as exactly as possible, phenolphthalein being used as indicator. When this solution was used with dilute aldehyde solutions, and tenth normal acid employed in the titration, the results obtained were quite far from the theoretical. This may, in part, be due to the difficulty of obtaining a sharp end point with sodium sulphite and tenth normal acid, 0.5 cc. acid, more or less, producing no effect on the end point. When, however, the concentrated aldehyde was used, normal or half normal acid could be used for the titration, and on ac-

[1] Ber. d. chem. Ges., **16,** 1333.
[2] *Ibid.*, **31,** 2979.
[3] Z. anal. Chem., **36,** 18.
[4] Ber. d. chem. Ges., **31,** 3317 (1898).
[5] Am. J. Pharm., **76,** 84 (1904). J. Soc. Chem. Ind., **23,** 303 (1904). J. Am. Chem. Soc., **27,** 1321 (1905).

count of the large amounts of acid used up, 0.1 or 0.2 cc. did not cause a serious error. The determination on formaldehyde was, therefore, carried out as follows:

Two to five grams of the 34 per cent. aldehyde solution were weighed into a stoppered Erlenmeyer flask and neutralized with tenth normal sodium hydroxide and 2 drops phenolphthalein; now 50 cc. of the neutral sodium sulphite solution were added for each 2 grams of aldehyde, the mixture allowed to stand about half an hour and titrated with half normal sulphuric acid to absence of a pink color. The amount of acid required by a blank containing an amount of sulphite equal to that left uncombined in the determination is subtracted from the amount required in the determination. This is the correction recommended by Russ[1] and Larsen. The results obtained by this method check very closely with those obtained by the bisulphite method, being almost identical with them. Sadtler,[2] however, in the case of citral, uses the same amount of sulphite as in the determination. He does not say whether that is also the condition in the case of formaldehyde. If, however, the blank contains the same amount of sulphite as the determination the results are about 0.75 per cent. less than those shown in Table II.

Benzaldehyde.—With benzaldehyde the conditions described in the Pharmacopoeia, 8th Revision, gave low results similar to those obtained with dilute solutions. As a result of comparative experiments in which the concentration of aldehyde, the amount of sulphite, the presence of alcohol or kerosene as diluent, and the interval before titration were the factors varied, the conditions which were found to be most satisfactory were as follows:

About a gram of benzaldehyde was weighed into a well-stoppered flask, 10 cc. alcohol added, then a little water, about 10 cc., to wash down the sides of the flask. The aldehyde was then neutralized with tenth normal alkali, 6 drops of 1 per cent. phenolphthalein being used as indicator. Then 50 cc. neutral sodium sulphite were added and titrated with half

[1] Mitt. Technol. Gewerb. Mus. Wien, [2] **18**, 85; Centralb., **1908**, II; 363.
[2] J. Soc. Chem. Ind., **23**, 303.

normal sulphuric acid until the pink color disappeared. A blank containing 35 cc. sulphite, the amount calculated to be left unabsorbed,[1] was carried out alongside of the determination, and the amount of acid required to render colorless subtracted from the total acid in the determination.

The alkali required to neutralize the aldehyde was calculated to benzoic acid and this weight of acid subtracted from the weight of the sample before calculating the per cent. of aldehyde. In this way results of about 99 per cent. of the theoretical were obtained for the benzaldehyde used.

A comparison of the results obtained under the Pharmacopoeia conditions and in the comparative experiments mentioned above will show the effect of increasing the amount of aldehyde and the superiority of the conditions selected over those of the Pharmacopoeia.

In the table below, the figures in Column A were obtained on 12 drops of the aldehyde as prescribed in the Pharmacopoeia.[2]

Table VI.—Comparison of Results with Neutral Sulphite on Benzaldehyde, under Various Conditions as Described Above

A Pharmacopoeia conditions Per cent.	B On small quantity of aldehyde Per cent.	C Pharmacopoeia conditions modified on 1 gram aldehyde Per cent.	D Under the author's conditions described above Per cent.
85.40	89.75	96.41	97.31
86.02	90.32	96.76	98.76
86.90	91.07	97.41	99.00
85.60	88.70	96.86	98.77
86.00		99.43	98.64
85.10		97.97	98.05
85.00		97.93	99.09
88.20		97.32	
90.10		97.10	
89.74			
88.17			
89.46			
86.00			

In Column B, the figures were obtained by employing the conditions described above on 12 drops of aldehyde. To

[1] Russ and Larsen: Centralb., **1908**, II, 363.

[2] Eighth revision.

confirm that the low results in Columns A and B were due to the small amount of material used, 1 gram aldehyde was substituted for the 12 drops and the determination carried out under the conditions prescribed in the Pharmacopoeia, 50 cc. sulphite solution being used instead of 10 cc. The results, which are quite conclusive, are shown in Column C. In the fourth column, D, the figures were obtained under the conditions prescribed above.

If, instead of titrating at once, the aldehyde is allowed to remain in contact with the sulphite, for a considerable period, the results obtained are low. Standing overnight gave figures between 83 and 86 per cent. instead of 98–99 per cent.

With salicylaldehyde and *p*-hydroxybenzaldehyde the acidity of the phenolic hydroxyl was neutralized with half normal sodium hydroxide and phenolphthalein before the sodium sulphite was added. During the neutralization or after the addition of the sulphite, colored compounds were formed which rendered it impossible to titrate with any degree of accuracy.

Anisic aldehyde behaves like benzaldehyde in that a clear solution is obtained which is not colored as with salicylaldehyde and *p*-hydroxybenzaldehyde. The determination of the end point is, however, more difficult; phenolphthalein must be added in the course of the titration, for the color is rather flitting.

The results that were obtained indicated only about 94 per cent. aldehyde when the determination was conducted under the conditions established under benzaldehyde.

In the case of vanillin, as with salicylaldehyde and *p*-hydroxybenzaldehyde, it was found very difficult to determine the end of the titration with any degree of accuracy whether the solution was titrated cold or hot. While the solution was only slightly colored when neutralized with sodium hydroxide on the addition of the sulphite, the brownish pink that developed could not be dissipated in the titration.

Attention may be directed here to the view of Seyewetz and Gibello.[1] They claim that when neutral sodium sulphite is

[1] Bull. soc. chim., [3] **31**, 691 (1904).

Table VII.—Results with Neutral Sulphite in Per Cent.

Formaldehyde[1] Per cent.	Benzaldehyde Per cent.	Salicylaldehyde Per cent.	*p*-Hydroxybenzaldehyde Per cent.	Anisic aldehyde Per cent.	Vanillin Per cent.
98.05	97.31	Not possible to determine with any degree of accuracy 52–54%	91.60	92.67	Not possible to determine with any degree of accuracy
98.64	98.76		89.60	94.09	
98.82	99.00		83.72	94.25	
98.11	98.77		83.18	93.46	
98.31	98.64		83.76	93.64	
98.00	98.05		76.09	92.33	
97.97	99.09		80.45	94.90	
98.70					
98.96	Av. 98.52				

Av. 98.40

added to formaldehyde, no reaction takes place until acid is added. The bisulphite then formed combines with the aldehyde. Since the formaldehyde bisulphite compound reacts neutral to phenolphthalein the sulphuric acid does not decolorize the indicator until all the formaldehyde has entered into combination with the bisulphite.

$$2Na_2SO_3 + 2CH_2O + H_2SO_4 = 2NaHSO_3.CH_2O + Na_2SO_4$$

The writer is inclined to agree with this explanation for the following reasons:

1. When sulphite is added to the aldehyde used, the characteristic odor of the latter is not dissipated even on long standing until acid has been added in sufficient amount to form bisulphite to combine with all the aldehyde present.

2. If during the titration the acid should be poured in quite rapidly with shaking, the solution will turn entirely colorless long before it should do so. On shaking for some time, however, it turns pink again and the titration can be continued: This is observed only slightly with formaldehyde, but is very marked with benzaldehyde and anisic aldehyde. The behavior described would seem to indicate that more bisulphite was formed than could be absorbed at once; on thorough agitation, however, the reaction proceeded to completion and all

[1] The results obtained by this method were 33.32 per cent. on the average and were divided by 33.86 per cent., which was the figure obtained as the average by the Romijin method. This was done in order to make the results comparable with the other columns.

the bisulphite present was eventually used up; the titration could then be continued.

3. In the course of the titration, the pink color does not seem to diminish much in intensity until very near the end.

In the case of benzaldehyde and anisic aldehyde it was, moreover, possible to get experimental proof of the absence of a reaction liberating alkali as follows:

Five cc. of the aldehyde were pipetted into a cassia flask filled to the divisions on the neck with neutral sodium sulphite. The benzaldehyde remaining on top, the amount added, could be readily measured so that the pipette reading was verified. After standing in this way for twelve days with frequent shaking it was observed that the aldehyde on top had not changed in amount. When 5 cc. of the clear sulphite solution were pipetted out from the bottom of the flask, 1.1 cc. half normal acid were required for neutralization, while a blank of 5 cc. sulphite required 1.15 cc. of the acid. No alkali was therefore liberated. The result was similar in the case of anisic aldehyde.

In the case of the sulphite method, a considerable amount of practice is required before the results will be uniform and concordant. Gildemeister and Hoffmann[1] say that it is impossible to titrate sulphite solutions sharply, so that the end point of the reaction can only be approximately determined. In spite of this disadvantage, for concentrated solutions the simplicity of the process and rapidity of execution make this method quite popular. As may be seen from Table IV, this method gives with formaldehyde results which are fairly uniform and slightly lower than those obtained by the iodine method. Benzaldehyde also may be determined with a fair degree of accuracy. With the other aldehydes studied this method gave results much below the truth.

THE CONVERSION OF ALDEHYDES INTO HYDRAZONES

A. Use of p-*Bromophenylhydrazine.*—J. Hanus[2] suggested the use of *p*-bromophenylhydrazine for precipitating vanillin quantitatively. An attempt was therefore made to apply this method to the other aldehydes.

[1] Die aetherischen Oele, 2nd Ed., p. 604.
[2] Z. Unters. Nahr. Genussm., **3**, 531 (1900).

The solutions used were approximately of 1 per cent. concentration; wherever possible water alone was used as the solvent or only as small a quantity of alcohol or acetic acid as would be required to keep the aldehyde in solution, when the desired concentration was obtained by diluting with water.

The precipitant was prepared fresh when required by dissolving in the necessary volume of hot water and filtering before use.

Attempts to precipitate formaldehyde with *p*-bromophenylhydrazine did not result successfully; the precipitate did not settle and ran through the filter.

With benzaldehyde under various conditions the results did not show more than about 93 per cent. of the aldehyde present. The hydrazone did not form well, was sticky and gave a rather turbid filtrate. Similarly the hydrazone obtained with salicylaldehyde resembled the benzaldehyde hydrazone and indicated only about 93 per cent. of the aldehyde.

A well-formed and easily handled hydrazone, however, was formed with *p*-hydroxybenzaldehyde; 25 cc. of a 1 per cent. solution of the crystals in water containing 40 cc. alcohol to the half liter were treated with 75 cc. hot water containing in solution 2–3 times as much hydrazine as will combine with the aldehyde to be precipitated.

The precipitation was conducted at 50° C. and the precipitate allowed to stand five hours. It was then filtered on a Gooch crucible, washed with hot water to absence of a reaction with silver nitrate and dried at 105°. The weight of the hydrazone multiplied by 0.4193 gives the weight of aldehyde present.

$$HOC_6H_4CHO + C_6H_4BrNHNH_2 = HOC_6H_4CH : NNHC_6H_4Br + H_2O$$

Theoretical results were obtained under the conditions described.

Anisic aldehyde gave results in the neighborhood of 99 per cent. when 1 per cent. of aldehyde in acetic acid (90 cc. glacial acid to half a liter) was used. The precipitation was

carried out under conditions similar to those described above with the exception that the precipitate was allowed to stand one hour instead of five and was dried at 100°. The weight of hydrazone multiplied by 0.4460 gives the aldehyde present.

The conditions for the precipitation of vanillin with *p*-bromophenylhydrazine are essentially as described by Hanus;[1] 0.5 gram of the hydrazine, being 2–3 times the theoretical amount, was dissolved in 75 cc. hot water, filtered, and added to 25 cc. of the 0.75–1.0 per cent. water solution of vanillin which was previously warmed. The temperature during the precipitation was kept at about 50° C. The precipitate settles in about half an hour and is allowed to stand for about five hours; it is then filtered on a Gooch crucible, washed with hot water until the washings no longer reduce silver nitrate, dried at 100°, and weighed.

The weight of the hydrazone multiplied by 0.4739 gives the weight of vanillin present.

Table VIII.—Percentage Results with p-*Bromophenylhydrazine*

Formaldehyde Per cent.	Benzaldehyde Per cent.	Salicylaldehyde Per cent.	*p*-Hydroxybenzaldehyde Per cent.	Anisic aldehyde[2] Per cent.	Vanillin Per cent.
A well	93.55	93.24	99.82	99.50	A—
defined	91.12	93.21	100.09	99.11	98.75
precipitate	91.92	93.04	99.88	99.09	98.50
did not	93.42	93.25			99.07
form	93.05	93.44			99.18
		94.35			B—
		94.25			98.88
					98.72
					99.21
					99.40
					99.37
					C—
					99.09
					99.32
					99.25
					99.02
					98.86
					98.81

[1] Z. Unters. Nahr. Genussm., **3**, 532 (1900).

[2] The results here were corrected for anisic acid by titrating 25 cc. with tenth normal alkali and substracting the weight of acid thus found from the weight of aldehyde present before calculating the per cent.

From the table it may be noticed that those aldehydes which were solid, vanillin and *p*-hydroxybenzaldehyde, tended to give hydrazones which were most suited for quantitative determination. The lower the molecular weights of those that are liquid, the further from being quantitative are the results.

B. The Use of p-*Nitrophenylhydrazine.*—W. Alberda, van Ekenstein and J. J. Blanksma[1] found that *p*-nitrophenylhydrazine precipitated acetone, acetaldehyde and benzaldehyde quantitatively. Although they give only single determinations in each case to support their contention, the method was considered promising and was taken up more fully with the aldehydes considered in order to ascertain how generally applicable it might be.

The solutions of the aldehydes employed here were the same as those used with *p*-bromophenylhydrazine. The precipitant was dissolved in 30 per cent. acetic acid or in dilute hydrochloric acid and the solution filtered. This was prepared fresh when wanted.

When this reagent was employed with formaldehyde, a well defined precipitate formed at once and was easily handled; the results, however, were much below those obtained by the other methods, showing only about 76 per cent. aldehyde.

As a result of various trials the conditions which gave the most consistent results with benzaldehyde were as follows:

A 1 per cent. solution of benzaldehyde in 12 per cent. acetic acid was prepared; 25 cc. of this solution were diluted with 50 cc. water and 30 cc. of 30 per cent. acetic acid containing about twice as much of the *p*-nitrophenylhydrazine as demanded by theory were added. The precipitate was allowed to stand five hours, then filtered on a Gooch crucible, washed with 10 per cent. acetic acid to absence of a strong color with dilute alkali, dried in an oven at 105°–110°, and the weight multiplied by 0.4400 to obtain the weight of benzaldehyde. If the weight of benzoic acid is separately determined, by titration with alkali, and subtracted from the weight of aldehyde taken for analysis, the method proves to be about 99 per cent.

[1] Rec. trav. chim., **24,** 33 (1905).

accurate. It is, therefore, the most accurate method for benzaldehyde at present known.

For salicylic aldehyde, the conditions which gave the most nearly quantitative results were essentially the same as for benzaldehyde:

To 20 cc. of a 1 per cent. solution of the aldehyde in 15 per cent. acetic acid were added 50 cc. of water and 25 cc. of 30 per cent. acetic acid containing 0.6 gram of the hydrazine. The precipitate was allowed to stand one hour, filtered on a Gooch crucible, washed with 10 per cent. acetic acid to absence of a strong color with dilute alkali, and dried at 105°–110°. The weight of the hydrazone multiplied by 0.4747 gives the weight of aldehyde present. The figures obtained under these conditions are quite concordant, though only about 95.5 per cent. of the theoretical.

When the conditions described above were applied to the determination of anisic aldehyde, *p*-hydroxybenzaldehyde and vanillin, the results obtained were about 100 per cent., 101.5 per cent. and 102 per cent. for the respective aldehydes. After considerable variation of conditions had been tried, the *p*-nitrophenylhydrazine was dissolved in very dilute hydrochloric acid of about normal strength and added drop by drop from a pipette to the aldehyde solution which had previously been diluted with 75 cc. water. The mixture was stirred vigorously while the precipitant was added, and the precipitate allowed to stand half an hour before filtration. It was washed on the Gooch crucible with a little of the dilute hydrochloric acid and finally with water until the washings gave only an opalescence with silver nitrate. Under these conditions both vanillin and *p*-hydroxybenzaldehyde gave theoretical results. The precipitant is most stable when kept cold, and coprecipitation is minimized by adding the reagent drop by drop. Anisic aldehyde, however, under the same conditions, gave results considerably below the theoretical. The greater solubility of this hydrazone (as well as its much lower melting point, which causes a loss through volatilization on drying) are probably responsible for the lower results. When the precipitation was repeated under the conditions established above in acetic

acid solution, the figures coincided with those previously obtained, coprecipitation and decomposition of the reagent counterbalancing the errors when hydrochloric acid was the solvent.

The factors for calculating the aldehyde from the weight of the respective hydrazones are 0.4747 for *p*-hydroxybenzaldehyde, 0.5019 for anisic aldehyde and 0.5353 for vanillin.

Table IX.—Percentage Results with p-*Nitrophenylhydrazine*

Formaldehyde	Benzaldehyde[2]	Salicylaldehyde	Anisic aldehyde[1]	*p*-Hydroxybenzaldehyde	Vanillin
75.81	98.63	95.16	96.35	100.00	100.00
	98.62	95.38	96.70	99.80	99.77
	98.71	95.36	96.35	99.46	100.19
	98.12	95.42	96.60	99.63	99.99
	99.42	min.	96.80		99.92
		figs.	96.32		99.92
		94.50			99.54
		94.63	96.54		99.94
			97.21		
			97.52		
			97.00		
			96.32		
			96.75		
			96.60		

The conditions recommended above for vanillin and *p*-hydroxybenzaldehyde were decided upon after experiments were carried out in which the amount of reagent, the temperature of precipitation, and the amount and variety of acid were varied.

Blank tests on the reagent proved that it remained clear for a longer period when kept cold, at room temperature, than when kept warm, at any higher temperature. When determinations were carried out in which the solutions were kept at room temperature throughout the work, theoretical results were obtained, and no signs of incomplete precipitation were noticed.

[1] See Table VIII for comparison of results on anisic aldehyde.

[2] The figures are corrected for the acid present as described above for benzaldehyde.

Table X.—Comparison of Results Obtained with Vanillin under a Few Different Conditions

Reagent dissolved in acetic acid.[1] Best conditions Per cent.	Reagent dissolved in hydrochloric acid: Reagent added in bulk Per cent.	Reagent added drop by drop: Solution kept warm Per cent.	Reagent added drop by drop: Solution kept cold Per cent.
102.53	101.58	101.66	100.00
102.68	101.35	101.21	99.77
102.48	101.12	100.94	100.19
102.68	101.91	100.54	99.99
102.18	101.85	100.88	99.92
102.14	101.62	100.31	99.92
102.18	101.70		99.54
102.20	101.50		
	101.82		

Table XI.—Comparison of Some Results Obtained with Anisic Aldehyde and p-Hydroxybenzaldehyde when the Reagent was Dissolved in Acetic Acid or Hydrochloric Acid and the Mode of Precipitation Varied

Aldehyde	Acetic acid solution under the best conditions Per cent.	Reagent dissolved in hydrochloric acid and added drop by drop: Solution kept warm Per cent.	Reagent dissolved in hydrochloric acid and added drop by drop: Solution kept cold Per cent.
	100.90	98.83	96.32
			96.54
	100.43	99.13	97.21
			97.52
	100.34	98.79	97.00
Anisic aldehyde[2]			96.32
	100.76	98.67	96.75
			96.60
	100.65	97.83	96.35
			96.70
	100.40		96.35
			96.60
			96.80
	101.82	101.12	100.00
p-Hydroxybenzaldehyde	101.68	100.95	99.80
	101.09		99.46
	101.51		99.63

[1] The conditions in which the amount of acid and the temperature and the amount of reagent used were essentially as described under benzaldehyde and had given results closer to the theoretical than had previously been obtained.

[2] Corrected for acid present as described above.

Table XII

Aldehyde	Iodine[1] Per cent.	Bisulphite Per cent	Neutral sulphite Per cent.	*p*-Bromo-phenylhydr. Per cent.	*p*-Nitro-phenylhydr. Per cent.	Alkalimetric[2] Per cent.
Formaldehyde	100.00	98.67	98.40	.....	75.81	.....
Benzaldehyde	.....	93.90	98.52	92.61	98.70	.....
Salicylaldehyde	.....	81.70	Not possible to determine with any degree of accuracy	93.54	95.33	.....
p-Hydroxybenzaldehyde	.....	87.39	87.48	99.93	99.72	.....
Anisic aldehyde	.....	90.16	93.62	99.23	100.58 (with acetic acid) 96.73	.....
Vanillin	.....	95.5	Not possible to determine with any degree of accuracy	99.03	99.90	99.06

[1] The average result obtained with the iodine method, 33.86 per cent., was called 100.00 per cent. and the results with the other methods calculated from that basis.

[2] The Wellman method for determining vanillin by titrating with alcoholic potash (Pharm. Ztg., **1898**, 634):

One gram of vanillin is introduced into a 200 cc. stoppered flask and 25 cc. alcohol and 25 cc. half normal alcoholic potash added; the excess of alkali is titrated with half normal acid and phenolphthalein. The strength of the alcoholic potash with the addition of alcohol is first determined, and the difference between the two titrations multiplied by 0.076 gives the weight of vanillin.

$$CH_3OC_6H_3(OH)CHO + KOH = CH_3OC_6H_3(OK)CHO + H_2O.$$

A table giving the average results of the aldehydes employed with the various methods is attached for purposes of comparison.

CONCLUSIONS

The aldehyde bisulphite compounds are resolved into their components by dilute acids or alkalies. This instability of the bisulphite compound is heightened by the presence of the hydroxy group in close proximity to the aldehyde group.

By means of the bisulphite method, formaldehyde may be quite accurately determined, the amount of vanillin and benzaldehyde approximately ascertained, while in the case of salicylaldehyde, *p*-hydroxybenzaldehyde and anisic aldehyde, the results show the method to be practically worthless.

In the cases tested, the aldehydes did not combine with the neutral sodium sulphite and liberate alkali as is generally believed, but a reaction is obtained when acid is added, indicating that bisulphite is then formed and combines with the aldehyde. Under the conditions given, formaldehyde and benzaldehyde may be determined with a fair degree of accuracy by means of sodium sulphite. The method, however, gave only approximate results with anisic aldehyde, and proved inapplicable to salicylaldehyde, *p*-hydroxybenzaldehyde and vanillin.

The sulphite method as here developed is shown to give more accurate determinations of benzaldehyde than does the method of the U. S. Pharmacopoeia.

p-Bromophenylhydrazine, on the other hand, was found to give quantitative results with anisic aldehyde, *p*-hydroxybenzaldehyde and vanillin, and not with formaldehyde, benzaldehyde and salicylaldehyde.

p-Nitrophenylhydrazine proved to be quite a general precipitant for aldehydes, yielding a well formed precipitate even with formaldehyde. This reagent is very suitable for determining vanillin and *p*-hydroxybenzaldehyde. With benzaldehyde, salicylaldehyde and anisic aldehyde, the results obtained are subject to errors of 2 to 4 per cent.

The precipitation methods were found to be more accurate than the volumetric determinations for vanillin, *p*-hydroxy-

benzaldehyde, salicylaldehyde and anisic aldehyde, while the volumetric methods gave better results with formaldehyde.

In the case of benzaldehyde both the volumetric sulphite method and precipitation with *p*-nitrophenylhydrazine gave results approximating the theoretical.

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NEW YORK CITY

ON THE REACTION OF ETHYL IODIDE WITH SODIUM 1-PHENYL-3-THIOURAZOLE

BY SIDNEY NIRDLINGER, F. M. ROGERS AND S. F. ACREE

[THIRTEENTH COMMUNICATION[1] ON CATALYSIS]

(We have been aided in these researches by the Carnegie Institution of Washington.)

In 1905–06 Brunel[2] and Acree began a quantitative study of the mechanism of the reactions of alkyl halides with urazoles by measuring the conductivities of a number of urazole salts and the velocities of their reactions with various alkyl halides. It was desired then to learn whether the alkyl halides react with the urazole anions or with the anions and cations together, or with the nonionized urazole salts. This information was desired not only for the sake of studying the relation

[1] This work was completed in May, 1908.

[2] THIS JOURNAL, **43**, 505, and especially **48**, 352.

of these reactions to catalysis and reaction mechanisms in general, but also in order to investigate, if possible, any relation that might be found between the mechanism of the reactions involved and the occurrence of the isomeric O-ether and N-ether which are always formed when the salts of the oxyurazoles are alkylated.

Our theory has contained from the beginning, as an essential element, *the idea that both the ionized*[1] *salts and the nonionized salts must be considered in all reactions of salts*, and this theory and our equations have recently been used successfully by us,[2] and also by Stieglitz,[3] to reinterpret his very fine experimental work on the Beckmann rearrangement and the hydrolysis of imido ester salts.

One of the substances investigated by Brunel was 1-phenyl-3-thiourazole, the study of which was continued by Shadinger[4] in 1905–07. We have used this as a starting point in the present investigation and have undertaken to measure the conductivity of the sodium salt and the velocity of its reaction with ethyl iodide in absolute ethyl alcohol. The conductivity measurements have been used as a basis for determining the per cent. of ionization of the salt, although we recognize that these results are probably somewhat in error on account of the change in the ionic velocities in the concentrated solutions resulting from complex ions, the variations in viscosity and especially from the changes in solvation of the hydrated salt used (see page 122), which Goldschmidt[5] and Lapworth[6] have shown in a number of fine papers, by several independent methods, to take place in alcoholic solutions. Although these changes in fluidity and solvation act in opposing directions in their effect on the ionic mobilities, these factors probably influence both

[1] For full references to the work of Bredig, Lapworth, Goldschmidt, Euler, Acree, and Stieglitz see Acree and Johnson: THIS JOURNAL, **38**, 258; **48**, 352.

[2] THIS JOURNAL, **48**, 368.

[3] J. Am. Chem. Soc., **34**, 1689, 1690.

[4] THIS JOURNAL, **39**, 226.

[5] Ber. d. chem. Ges., **28**, 3218; **29**, 2208; **39**, 711. Z. physik. Chem., **60**, 728; **70**, 627; **81**, 30. Z. Elek. Chem., **15**, 4, 305, 740; **17**, 684.

[6] J. Chem. Soc., **93**, 2203; **97**, 21; **99**, 1417, 2224; **101**, 2249. See also the important researches of H. C. Jones and coworkers on aqueous solutions.

the conductivities and the reaction velocities, and are being investigated.

The velocity of the reaction was determined by measuring at any time, t, the concentration $(A-x)$ of the urazole salt by titrating it with a standard solution of iodine. The iodine reacts quantitatively with the sodium thiourazole according to the equation:

$$2C_6H_5N_3C_2OHSNa + I_2 \longrightarrow 2NaI + (C_6H_5N_3C_2OHS)_2$$

the end point being very sharp in the presence of starch.[1] The concentration of the alkyl halide was represented by $(B-x)$.

The data thus secured were substituted in a general equation, discussed in other articles,[2] having such a form that we can tell at once whether the urazole anions, or anions and cations together, or the nonionized urazole salts are reacting with the alkyl halide. The equation has the form (*a*) or (*b*):

$$(a)\quad \frac{dx}{dt} = K_s\alpha(A-x)(B-x) + K_m(1-\alpha)(A-x)(B-x)$$
$$= [K_s\alpha + K_m(1-\alpha)](A-x)(B-x)$$

or

$$(b)\quad \frac{dx}{dt} = K_s\alpha(A-x)(B-x) + K_m\frac{\alpha^2}{V}(A-x)(B-x)$$
$$= \left[K_s\alpha + K_m\frac{\alpha^2}{V}\right](A-x)(B-x)$$

Therefore,

$$(a)\quad VK_V = K_n = K_s\alpha + K_m(1-\alpha)$$

or

$$(b)\quad VK_V = K_n = K_s\alpha + K_m\frac{\alpha^2}{V}$$

for *normal solutions* when $1/V$ is the concentration of the sodium phenylthiourazole. Equation (*b*) also represents the reaction as one of the anions alone, accelerated by the cations. As has been discussed before, when the data are substituted in the integral of (*a*) very good constants are obtained for both K_s and K_m, the average value of K_s being 0.435 and that for K_m being 0.17. The use of the integral of (*b*) leads to no con-

[1] Shadinger and Acree: THIS JOURNAL, **39**, 259, 260.

[2] See THIS JOURNAL, **38**, 258; **43**, 518; **48**, 353.

stants and we can therefore conclude that the velocity of the reaction of the sodium salt of 1-phenyl-3-thiourazole with ethyl iodide is a function of the concentration of the anions of the urazole as well as of the concentration of the nonionized sodium urazole salt:

(1) $C_6H_5N_3C_2OHSNa + IC_2H_5 \longrightarrow C_6H_5N_3C_2OHSC_2H_5 + \overset{+}{Na} + \overset{-}{I}$

(2) $C_6H_5N_3C_2OH\overset{-}{S} + IC_2H_5 \longrightarrow C_6H_5N_3C_2OHSC_2H_5 + \overset{-}{I}$

The ratio $K_i : K_m$ is approximately 2.5, and we can therefore say that the anions are 2.5 times as effective in the reaction as the nonionized sodium salt. This is entirely in harmony with the reactions of ethyl iodide with sodium phenolate and sodium ethylate at 25°, the ratio $K_i : K_m = 5.65$ holding for the former and $K_i : K_m = 2.8$ having been found for sodium ethylate.[1]

The K_i and K_m used here may be the sum or product of other constants and hence may include "abnormal salt effects" of ions or molecules, a factor for viscosity, etc. Although the "abnormal salt effect"[2] seems fortunately to be small in this case, its value will be determined accurately by studying the reaction in very dilute solutions in which such physical factors as viscosity, "abnormal salt effect," etc., seem to play a very small role. This question, however, is being investigated thoroughly.

Dr. J. Chandler has continued the study of this reaction by using the anhydrous sodium urazole salt in absolute ethyl alcohol under somewhat different experimental conditions, and has found the values $K_i = 0.465$ and $K_m = 0.16$. Our slightly lower values for the reaction velocities are due to *our larger experimental errors* and to the use of the *hydrated* urazole salt, and therefore to the presence of small quantities of water, which lowers the reaction velocity. Dr. Chandler has found that the addition of sodium iodide suppresses the ionization

[1] Shrader, Robertson and Marshall: THIS JOURNAL, **48**, 352, 378.

[2] The "normal salt effect" is the change in the velocity of transformation of the active salt resulting from the variation in ionization accompanying changes in its concentration or the addition of another salt. We call any *additional* change in reaction velocity an "abnormal salt effect."

and reaction velocity of the sodium phenylthiourazole practically exactly the amount calculated from our theory; the "salt effect" is "normal" even when three equivalents of sodium iodide are added to one of the sodium phenylthiourazole (N/64).

Salt Catalysis

It is thus seen that the above reaction is *chiefly*, though not purely, ionic, and hence that the reaction velocity is not strictly proportional to the concentration of the ions. We have explained this deviation as due *chiefly* to the activity of the *nonionized salts*, augmented by a small "abnormal salt catalysis" resulting from changes in the physical properties of the solution, and perhaps to double compounds. In another case, that of the rearrangement of the acylhalogenaminobenzene derivatives,[1] the reaction seems to involve practically *only* the *nonionized salt*. We thus see that there are other cases in which the reactions are *chiefly*, but not necessarily entirely, *nonionic* in character, the *deviation* being due *chiefly* to the activity of the *ionized* salt, augmented perhaps by an "abnormal salt catalysis." We have already found the relative importance of the ionic and the nonionic reactions to vary very greatly with different cases. In his fine work on imido esters Stieglitz[2] noted a similar deviation from the purely ionic reaction, and used as an explanation the Arrhenius-Euler theory that the imido ester salts exert an "auto salt effect" on the reaction because they change the per cent. of ionization of the water, which was assumed to react through its ions alone.

(3) $C_6H_5C(:\overset{+}{N}H_2)OCH_3 + \overset{+}{H} + \overset{-}{O}H \longrightarrow$

$C_6H_5COOCH_3 + \overset{+}{N}H_4$

Our work[3] and his[4] data, and those of Van Dam[5] on the Beckmann rearrangement, have shown that Stieglitz's explana-

[1] THIS JOURNAL, **37**, 410; **38**, 265; **41**, 464; **48**, 364.
[2] *Ibid.*, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32**, 221; **34**, 1687.
[3] See especially THIS JOURNAL, **38**, 258; **39**, 513; **48**, 352.
[4] J. Am. Chem. Soc., **34**, 1689, 1690.
[5] Rec. trav. chim., **18**, 408; **19**, 318.

tion is not wholly satisfactory. He now finds[1] that he can reinterpret both the imido ester work and the Beckmann rearrangement as *reactions of both ions and nonionized salts*, augmented by a salt catalysis proportional to the concentration of the total salt present. He has shown that our equations accord excellently with his data. Our results, however, on the reactions of alkyl halides with phenolates, ethylates, etc., show that all previous interpretations of *salt catalysis* advanced by others must be modified. Especially would we emphasize the fact that *our* "abnormal salt effect" is in certain cases a function not only of the concentrations of the inactive salts present but also of the concentrations of the reacting substances, as expressed in the equation:

$$\frac{dx}{dt} = [1 + (f)C_{salt}][K_i\alpha + K_m(1-\alpha)](C_{salt} - x)(C_{alkyl\ halide} - x)$$

We would also call attention to the fact that the assumption that the water reacts through its ions *alone*, which were assumed to be increased in concentration by the addition of salts, is not advocated by Lapworth[2] or the writers,[3] and is not in harmony with three well known classes of facts, which have been discussed more fully by us elsewhere.[4]

(1) The same salt in the same concentration must be assumed by these colleagues to increase K_w in some cases and decrease it in others.

(2) The work of Lorenz[5] and Böhi on the hydrogen electrode and that of Kohlrausch show the ionization of water to be practically constant, whether salts, acids or bases are present or not.

(3) The value of K_w increases rapidly with a rise in temperature and the increase in the velocity of the reaction (3) with rise in temperature should involve the factor resulting from the increase in the active mass of the water as well as the factor due to the normal acceleration of the reaction through rise in temperature, which is independent of the changes in con-

[1] J. Am. Chem. Soc., **34**, 1689, 1690, 1694.
[2] Chem. News, **97**, 310. J. Chem. Soc., **93**, 2196.
[3] This Journal, **41**, 475; **48**, 369.
[4] *Ibid.*, **41**, 475; **48**, 368–372.
[5] Z. physik. Chem., **66**, 733.

centration. As a matter of fact, the temperature coefficients of the hydrolysis of imido ester salts[1] and acetamide[2] are only normal in magnitude when the active mass of the ionized portion of the water is left out of consideration altogether. The corresponding temperature coefficient for cane sugar[3] is rather large, although part of this may be due to changes in viscosity and to other abnormal physical properties which Morse and Frazer[4] showed prevent the strict application of the laws for ideal solutions. It may well be, then, that cane sugar reacts partly with the molecular water and partly with the hydroxyl and hydrogen ions together. More data for very dilute solutions of cane sugar would help us to ascertain the influence that viscosity exercises on the reaction velocities. Similar data for the hydrolysis of esters by acids would be very helpful.

We can all agree, then, that the "salt effect" is a very complicated phenomenon varying in nature in different cases, of which the true underlying principles can be learned only by the very accurate data now being collected by the different workers. In his study of the catalytic action of ethylates on the addition of alcohol to *p*-bromobenzonitrile Dr. C. N. Myers has found that there is apparently no "abnormal salt effect" noticed in the dilute solutions (N/32 to N/2048), this factor becoming measurable only in the more concentrated solutions (N/8 to N/32). We are now especially attempting to use the electron theory[5] to guide us in correlating our data and predicting other relationships. *We do not believe that chemists have yet discovered the fundamental laws which explain "how and why" chemical reactions take place. The idea that both ions and non-ionized compounds react is therefore presented only tentatively, as are all theories, pending the final reports.*

EXPERIMENTAL

Sodium Salt of 1-Phenylthiourazole.—The phenylthiourazole was made in the way described by Shadinger, and was recrys-

[1] Derby: THIS JOURNAL, **39**, 470–1.
[2] Ostwald: J. prakt. Chem., [2] **27**, 25. Crocker: J. Chem. Soc., **91**, 603.
[3] J. Spohr: J. prakt. Chem., [2] **32**, 32. Euler: Z. physik. Chem., **32**, 348.
[4] THIS JOURNAL, **34**, 28; **45**, 29.
[5] Acree: THIS JOURNAL, **45**, 372.

tallized quickly from hot alcohol until it melted sharply at 195°. This acid was then titrated with the exact equivalent of sodium bicarbonate in a hot solution and the solution was evaporated to a small volume. The sodium salt crystallizes well with 3 molecules of water of crystallization. As only one molecule of water, approximately, is removed at 110°, and a small amount of decomposition was noticed, the hydrated salt was crystallized several times from alcohol and used for all the work. The theoretical amount of water in this salt is 20.07 per cent.; an analysis of one sample by the sodium sulphate method gave 20.28 per cent., and analyses of two other samples by the iodine method (see below) gave 19.68 and 20.02 per cent., respectively.

Absolute Ethyl Alcohol.—This solvent was prepared from commercial 95 per cent. alcohol which was boiled with lime two days, distilled, allowed to stand over lime four days and distilled again, and then fractionated carefully. The alcohol contained probably not over 0.05 per cent. of water. A portion was obtained whose boiling point did not vary more than 0°.05, and whose conductivity ranged from 0.22×10^{-6} to 0.27×10^{-6}; this was used in the conductivity work. The remainder of the alcohol, which had a conductivity of 0.46×10^{-6}, was used in the reaction velocities. The ethyl iodide was carefully purified.

Conductivity Apparatus.—The bridge wire, resistance box and cells were very carefully calibrated just before the work was begun. The cells were sufficiently constant in resistance when 0.02 N potassium chloride solutions were used to standardize them; the molecular conductivity of this solution was assumed to be 129.8.

Analytical Methods.—The standard solutions of iodine and sodium thiosulphate were checked carefully against weighed portions of pure iodine and pure 1-phenyl-3-thiourazole neutralized exactly with an alkali in the presence of phenolphthalein.

The solutions of the sodium thiourazole were first made separately at 25°. Ten cc. of the urazole solution were pipetted

into 50 cc. water and titrated with the standard solution of iodine to determine the value of A', starch being added toward the end of the titration. The reaction takes place quantitatively as follows:

$$2C_6H_5N_3C_2OHSNa + I_2 \longrightarrow 2NaI + (C_6H_5N_3C_2OHS)_2$$

The solution of the ethyl iodide was then made at 25°, exactly equivalent to the solution of the urazole salt. Ten cc. portions of the urazole solution were pipetted into 20 cc. flasks and 10 cc. portions of the ethyl iodide solution carefully pipetted into these, both solutions being initially at 25°. At various intervals of time, t, the contents of the flasks were poured into 50 cc. of water, and the concentration of the urazole salt, $(A' - x)$, was determined by titration with the standard solution of iodine.

When the concentration, A', of the solution of the sodium thiourazole was not exactly that desired the proper correction was made in K_V, as can be seen in the tables. From the corrected value A, K_V and K_n were calculated according to Equation (*a*) in the introduction. The values of K_i and K_m were calculated from the series of simultaneous equations,

$$K_n = K_i\alpha + K_m(1 - \alpha)$$
$$K'_n = K_i\alpha' + K_m(1 - \alpha')$$
$$K''_n = K_i\alpha'' + K_m(1 - \alpha''), \text{ etc.}$$

and these are given in Table VIII. The values of K_i and K_m are quite constant, whereas the integral of Equation (*b*) leads to values of K_i and K_m that are not at all constant.

Table I.—0.3 N Sodium 1-Phenyl-3-thiourazole + 0.3 N Ethyl Iodide

t	A'	$A' - x$	x	$K'V$
10	53.08	30.92	22.16	0.0716
15	53.08	25.65	27.43	0.0713
20	53.08	22.26	30.82	0.0692
25	53.08	19.46	33.62	0.0691
30	53.08	17.49	35.59	0.0678
40	53.08	14.40	38.68	0.0671

$A = 52.54$, $K_V = 0.0687$, $K_n = 0.229$ Mean, 0.0694

Table II.—0.2 N Sodium 1-Phenyl-3-thiourazole + 0.2 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
10	34.94	22.88	12.06	0.0527
15	34.94	19.63	15.31	0.0520
20	34.94	17.03	17.91	0.0526
25	34.94	14.96	19.98	0.0534
35	34.94	12.45	22.49	0.0516
60	34.94	8.45	26.49	0.0522

$A = 35.03$, $K_V = 0.0524$, $K_n = 0.262$ **Mean, 0.0524**

Table III.—0.1 N Sodium 1-Phenyl-3-thiourazole + 0.1 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
15	17.47	12.19	5.28	0.0288
25	17.47	10.23	7.24	0.0283
35	17.47	8.85	8.62	0.0278
45	17.47	7.71	9.76	0.0281
60	17.47	6.28	11.19	0.0296
90	17.47	5.10	12.37	0.0269

$A = 17.51$, $K_V = 0.0283$, $K_n = 0.283$ **Mean, 0.0283**

Table IV.—0.05 N Sodium 1-Phenyl-3-thiourazole + 0.05 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
20	8.74	6.55	2.19	0.0167
30	8.74	6.07	2.67	0.0146
45	8.74	5.16	3.58	0.0154
60	8.74	4.50	4.24	0.0157
90	8.74	3.73	5.01	0.0149
120	8.74	3.14	5.60	0.0148

$A = 8.76$, $K_V = 0.0154$, $K_n = 0.308$ **Mean, 0.0154**

Table V.—0.025 N Sodium 1-Phenyl-3-thiourazole + 0.025 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
30	4.23	3.45	0.78	0.0078
60	4.23	2.88	1.35	0.0078
90	4.23	2.61	1.62	0.0069
120	4.23	2.23	2.00	0.0075
210	4.23	1.51	2.72	0.0085
300	4.23	1.26	2.97	0.0079

$A = 4.38$, $K^V = 0.0080$, $K_n = 0.320$ **Mean, 0.0077**

Table VI

V	3.33	5.0	10.0	20.0	40.0
K_n	0.229	0.262	0.283	0.308	0.320

Table VII.—Conductivities of the Sodium Salt of 1-Phenyl-3-thiourazole in Ethyl Alcohol at 25°

			α		$1-\alpha$	
V	μ_V (1)	μ_V (2)	(1)	(2)	(1)	(2)
3.33	9.08	9.23	27.25	27.7	72.75	72.3
5.0	10.79	10.88	32.4	32.6	67.6	67.4
6.67	12.09	...	36.3	....	63.7	....
10.0	14.04	14.26	42.1	42.7	57.9	47.3
20.0	17.61	17.44	52.8	52.4	47.2	47.6
40.0	19.11	19.49	57.3	58.5	42.7	41.5

$\mu_\infty = 33.3$

Table VIII

	K_i		K_m	
	(1)	(2)	(1)	(2)
$V = 3.33 : 10$	0.49	0.48	0.14	0.13
$V = 3.33 : 20$	0.45	0.46	0.15	0.14
$V = 3.33 : 40$	0.45	0.44	0.15	0.15
$V = 5 : 10$	0.41	0.40	0.19	0.19
$V = 5 : 20$	0.41	0.42	0.19	0.19
$V = 5 : 40$	0.42	0.41	0.185	0.19
$V = 10 : 20$	0.42	0.44	0.185	(0.27)
$V = 10 : 40$	0.42	0.42	0.180	0.18
$V = 20 : 40$	0.45	0.40	0.17	0.20
Average,	0.435	0.43 Av.	0.17	0.17

$K_i : K_m = 2.5$

SUMMARY

(1) The velocity of the reaction of ethyl iodide and sodium 1-phenyl-3-thiourazole has been measured in solutions varying from 0.3 N to 0.025 N. The per cent. of ionization of the sodium salt was measured at the same concentrations by the conductivity method.

(2) The data obtained were substituted in the equation $K_n = K_i\alpha + K_m\ (1-\alpha)$, and satisfactory constants were obtained for K_i and K_m. The conclusion is that the reaction velocity is, in this case, a function of the concentrations of

both the urazole ions and the nonionized urazole salt. While this conclusion is presented only tentatively pending our final report, a large amount of data secured from work with ethylates, phenolates, nitriles and other compounds harmonizes with this point of view. The influence of *auto* and other "salt effects" will be discussed in the completed articles.

JOHNS HOPKINS UNIVERSITY
May 1, 1908

ON THE REVERSIBLE ADDITION OF ALCOHOLS TO NITRILES CATALYZED BY ETHYLATES. I

BY E. K. MARSHALL, JR., AND S. F. ACREE

[FOURTEENTH[1] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

In connection with the studies of catalysis carried on in this laboratory we have undertaken a series of investigations dealing with the chemical action of the ethylates of sodium, potassium, lithium, thallium and other metals in absolute ethyl alcohol on various organic compounds. E. K. Marshall, Jr., H. C. Robertson, Jr., J. H. Shrader, Miss B. M. Brown and Dr. Julia P. Harrison have found that sodium, potassium and lithium ethylates react with alkyl halides and form ethers and sodium halides by bimolecular reactions which seem to involve *both the ethylate ions*[2] *and the nonionized ethylate salt*.[3]

$$C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + \overset{+}{Na} + \overline{I}$$

$$C_2H_5\overline{O} + IC_2H_5 \longrightarrow (C_2H_5)_2O + \overline{I}$$

Robertson and Shrader[4] showed that sodium, potassium and lithium phenolates react with alkyl halides and form phenol ethers in exactly the same way, *both the nonionized phenolate salts and the phenolate ions apparently reacting with the alkyl*

[1] THIS JOURNAL, **27**, 118; **28**, 370; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258, 489, 746; **39**, 124, 145, 226, 300; **41**, 457, 483; **42**, 115; **43**, 358, 505; **44**, 219; **48**, 352; **49**, 116. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **38**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909). J. Am. Chem. Soc., **30**, 1755.

[2] For references to the work of Bredig, Lapworth, Goldschmidt, Euler, Acree, and Stieglitz, see THIS JOURNAL, **38**, 258; **48**, 352.

[3] See especially THIS JOURNAL, **48**, 353, 378.

[4] *Ibid.*, **48**, 357, 378.

halide. F. M. Rogers, Sidney Nirdlinger[1] and J. Chandler have shown that *ethyl iodide reacts with the nonionized sodium salt of 1-phenyl-3-thiourazole, as well as with the urazole anion.* The conductivity and ionization of all these salts have been measured by H. C. Robertson, Jr., in solutions varying in concentration from N/1 to N/16000, and the velocity of the reactions was measured in solutions varying from N/1 to N/32 or N/64. The "normal"[2] and "abnormal" "salt effects" have been measured by adding known quantities of sodium iodide, sodium bromide, potassium iodide and potassium bromide to these solutions, the ionization of the separate salts and of the mixtures having been accurately measured by Dr. Robertson. The details of all these investigations will appear in due time, after such physical factors as viscosity, solvation, double compounds and electronic phenomena have been investigated more fully.

It will be observed, however, that in all of these reactions the ethylate, phenolate and urazole salt are transformed into the end product, these being cases of "pseudo catalysis." We have therefore desired to study a number of cases in which the ethylate salts bring about their transformations "purely catalytically" and are not appreciably used up in the process, such studies being very desirable in order to learn whether the mechanism of the reaction of the ethylate is the same in "pure catalysis"[3] as in "pseudo catalysis" and involves both the ethylate ions and the nonionized ethylate salts. Such a case of "pure catalysis" has been worked out beautifully by Tubandt[4] in his investigation of the reversible inversion of *d*- and *l*-menthone by sodium ethylate, and we have shown[5] that his data give excellent evidence that *both the ethylate ions and the nonionized sodium ethylate are equally active in the inversion of the menthone.*

[1] THIS JOURNAL, **48**, 358, 378; **49**, 116.

[2] The "normal salt effect" is the change in the velocity of transformation of the active salt resulting from the variation in ionization accompanying changes in its concentration on the addition of another salt. We call any *additional* change in reaction velocity an "abnormal salt effect."

[3] See THIS JOURNAL, **48**, 362, and earlier papers for a full discussion of this subject.

[4] Ann. Chem. (Liebig), **339**, 41; **384**, 259; **377**, 284.

[5] THIS JOURNAL, **48**, 359.

We have wished to take up other cases of such reversible reactions to learn whether the two opposing reactions are accelerated to the same extent by the ethylate ions and the nonionized ethylate salts; in other words, to learn whether the ratio $K_i : K_m$ is the same for the opposing reactions. In continuation of the reaction of hydroxylamine with carbonyl compounds,[1] which is accelerated by ethylates, Dr. E. K. Marshall, Jr., is studying the addition of ammonia and its substitution products, hydroxylamine, etc., to unsaturated compounds and in particular the reversible reaction,

$$RN : CS + R'NH_2 \rightleftarrows RNHCSNHR'$$

In general, the reaction goes too far toward the right to be studied accurately *from both sides* as a reversible reaction, and Dr. Marshall has found that *the velocity is not changed by the addition of ethylates, ammonium bromide or ammonium iodide.* This shows that the amines do not react with the mustard oils through their amide ions alone, $\bar{N}H_2$,

$$\overset{+}{N}a + \bar{O}C_2H_5 + NH_3 \rightleftarrows \overset{+}{N}a + \bar{N}H_2 + HOC_2H_5$$

$$2NH_3 \rightleftarrows \overset{+}{N}H_4 + \bar{N}H_2$$

but rather as NH_3 or possibly *both* its ions, a result also in harmony with our data on the reaction of ammonia with ethyl formate,

$$(HCOOC_2H_5 + NH_3 \rightleftarrows HCOOC_2H_5.\overset{+}{H} + \bar{N}H_2) \longrightarrow HCONH_2 + C_2H_5OH$$

as against

$$(HCOOC_2H_5 + \overset{+}{N}H_4 \rightleftarrows HCOOC_2H_5 + \overset{+}{H} + NH_3 \rightleftarrows HCOOC_2H_5.\overset{+}{H} + NH_3) \longrightarrow HCONH_2 + \overset{+}{H} + C_2H_5OH$$

the velocity of which is not appreciably changed by the addition of ammonium chloride.[2] The details of this work will appear shortly.

Another class of reactions which we have undertaken to study are those involving the reversible (or irreversible) addition of alco-

[1] This Journal, **38**, 308; **39**, 300. Desha: Diss., Johns Hopkins Univ., 1907.

[2] See also Stieglitz: J. Am. Chem. Soc., **32**, 230.

hols to unsaturated compounds, especially those catalyzed by ethylates.[1] Dr. Marshall has begun to investigate the reversible addition of alcohol to mustard oils, a transformation which is enormously accelerated by ethylates.[2] Another similar case which should be investigated is the addition of alcohols to olefins, such as acrylic, crotonic, maleic and fumaric esters,[3] a reaction generally proceeding too slowly to be detected except when catalyzed by ethylates. Friedländer[4] and Mähly found, however, that the compounds *m*- and *p*-$NO_2C_6H_4CH : C(NO_2)COOCH_3$ and the ethyl esters add methyl alcohol and ethyl alcohol without the aid of ethylates, and yield such products as

$$NO_2C_6H_4CH(OC_2H_5)CH(NO_2)COOCH_3$$

An excellent reaction for study in this connection is the reversible addition of alcohols to nitriles, catalyzed by ethylates and methylates. The nitriles studied by us do not add alcohols with any appreciable velocity unless catalyzed by acids or ethylates, as special experiments have uniformly shown. The idea that all nitriles may add alcohol in the presence of ethylates is merely an extension of the work of Purdie[5] on the fumaric and maleic acid esters, of Wurtz,[5] Hofmann,[5] Schiff,[5] and others, on the isocyanates and mustard oils, of Kremann,[6] Claisen,[7] Kossel,[8] and others, on esterifications by ethylates,

$$C_6H_5COOCH_3 + NaOC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + NaOCH_3$$

of Stieglitz[9] and Dains on the carbodiimides, and especially of Nef on the nitriles,[10] and of Stieglitz[11] and McKee, and of

[1] Professor Stieglitz has written me that he too has for several years believed that the activity of the ethylates in all such reactions would be found to depend upon the "electrical conditions" of the solutions.

[2] Hofmann: Ber. d. chem. Ges., **2**, 120; **3**, 772. Bamberger: *Ibid.*, **15**, 2164. Schiff: *Ibid.*, **9**, 1316. Wurtz: Ann. chim phys., [3] **42**, 43.

[3] Purdie: J. Chem. Soc., **39**, 344; **47**, 863, 867; **59**, 469.

[4] Ann. Chem. (Liebig), **229**, 210.

[5] *Loc. cit.*

[6] Kremann: Monats. Chem., **26**, 783; **29**, 23.

[7] Claisen: Ber. d. chem. Ges., **20**, 646.

[8] Kossel, Krüger and Obermüller: Z. physiol. Chem., **15**, 321: **16**, 153.

[9] Dains: J. Am. Chem. Soc., **31**, 136.

[10] Nef: Ann. Chem. (Liebig), **287**, 280.

[11] McKee: THIS JOURNAL, **36**, 206.

McKee,[1] on the addition of alcohols to cyanoamides in the presence of the corresponding alcoholates:

$$R_2NCN + HOC_2H_5 \longrightarrow R_2NC(:NH)OC_2H_5$$

We have never seen a statement that the reverse reaction, the decomposition of an imido ester into the nitrile and the alcohol, takes place in alcohol in the presence of ethylates, although imido esters are decomposed in this way in water by alkalies.[2] It was this general parallelism in the reactivity of sodium ethylate and sodium hydroxide that made us suspect that sodium ethylate would cause imido esters to decompose into nitriles and alcohols.

In every case examined we have found the reaction to be reversible. The equilibrium point is the same whether measured from the nitrile or the imido ester, although slow disturbing side reactions make the agreement in some cases less satisfactory than desired. The equilibrium point varies very widely with the different compounds. The per cent. of imido ester formed is illustrated by the following examples: butyronitrile, 0.90; propionitrile, 1.75; acetonitrile, 2.50; *p*-tolunitrile, 6.8; benzonitrile, 14.0; *p*-bromobenzonitrile, 27.2; *m*-bromobenzonitrile, 38.0; *p*-nitrobenzonitrile, 62.0; *m*-nitrobenzonitrile, 78.0; diisoamylcyanoamide, 98.0. The equilibrium point varies rather widely in some cases with changes in the concentrations of the nitrile and the ethylate, but fluctuates very little in other examples. Different ethylates catalyze the reaction with different velocities and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, the *p*-nitrobenzonitrile reacting very rapidly, whereas *o*-tolunitrile hardly adds alcohol at all.

Stieglitz and Schlesinger[3] found that barium hydroxide causes the decomposition of imido esters *in water* into nitriles and alcohols, and they interpreted their results on the Ostwald-Arrhenius hypothesis that the decomposition is due to the hydroxyl ions *alone*, as in the case of the saponification

[1] McKee: THIS JOURNAL, **36**, 209; **42**, 1.
[2] See especially a fine study by Stieglitz and Schlesinger: THIS JOURNAL, **39**, 738.
[3] Stieglitz and Schlesinger: THIS JOURNAL, **39**, 738.

of ordinary esters by hydroxides. But we[1] have recalculated their excellent data and have found that the concentration of the barium hydroxide molecules is so small, about three to seven per cent., that *their results can be reinterpreted fully as well on our theory that both the hydroxyl ions and the nonionized barium hydroxide are, in this case, equally active.* Our theory, then, applies equally well to their work and to ours, whereas their[2] theory that only the hydroxyl ions (or the ethylate ions, in our case) are active does not at all agree with our work on the ethylates, as the following discussion will show.

Having learned that the reaction is reversible, we have begun the quantitative study of several cases to learn whether the ethylate ions and the nonionized sodium, potassium, and lithium ethylates catalyze both of the reverse reactions exactly alike; that is, whether the ratio $K_i : K_m$ is the same for the opposing reactions. Dr. E. K. Marshall has learned that sodium ethylate, in concentrations varying from N/4 to N/64, causes the decomposition of N/4 acetimido ethyl ester with the velocities $K_i = 0.344$ and $K_m = 0.228$. Dr. Julia P. Harrison showed that sodium ethylate, in concentrations varying from N/4 to N/64, causes the decomposition of N/4 benzimido ethyl ester with the velocities $K_i = 0.1148$ and $K_m = 0.1003$. Dr. Marshall and Dr. Harrison have shown that added sodium iodide lowers the per cent. of ionization and the reaction velocity "normally," or to just the extent calculated from our theory. Dr. C. N. Myers has studied the reversible addition of ethyl alcohol to 0.15 N *p*-bromobenzonitrile in the presence of sodium ethylate varying in concentration from N/8 to N/2048 N and has found that the ethylate ions and the nonionized sodium ethylate are about equally active and act purely catalytically. Of especial importance is the fact that there is no "abnormal salt effect" by the ethylate noticed in the very dilute solutions

[1] Acree: THIS JOURNAL, **48**, 359.

[2] Stieglitz now finds (J. Am. Chem. Soc., **34**, 1689, 1690, 1694) that he can reinterpret both the imido ester work and the Beckmann rearrangement as *reactions of both ions and nonionized* salts, augmented by a salt catalysis proportional to the concentration of the total salt present. We had pointed out 4 years ago that the nonionized imido ester salts should be considered (THIS JOURNAL, **39**, 521; and especially *Ibid.*, **48**, 368).

(N/32 to N/2048), this factor becoming appreciable only in the more concentrated solutions (N/8 to N/32). In these *ideal* solutions the value for K_i for the *ethylate ion* is the same for both sodium ethylate and lithium ethylate, but the values for K_m for the *nonionized* sodium ethylate and lithium ethylate are considerably different, in accordance with our theory. We consider this work on the *p*-bromobenzonitrile to be our first *complete proof* of the *simultaneous activity of ions and nonionized* salts, because these *ideal* solutions are free from the abnormal physical properties which make the interpretation of the data for concentrated solutions less rigorous. All of these investigations will be published in due time when the action of sodium, potassium and lithium ethylates on several nitriles, and the reverse reactions, have been studied in widely varying concentrations, in the presence of different amounts of added salts and at different temperatures. The effect of certain physical factors will be especially investigated.

EXPERIMENTAL

The bath used in this work was a large one, which has been used for some time in this laboratory in investigations on reaction velocities and will be fully described elsewhere. Its temperature was constant at 25° to within ±0°.005.

The *absolute alcohol* was prepared by distillation from lime. The amount of water remaining in the alcohol was never more than 0.03 per cent. Generally, it contained considerably less than this, as was determined by careful specific gravity estimations. The solutions of sodium ethylate were prepared very carefully by a method which will be described in the work on the "Reactions between Sodium Ethylate and Alkyl Halides," soon to be published. The solutions of the nitriles were prepared by weighing into a flask containing alcohol a little more than the required amount, diluting to the mark, and then measuring in sufficient alcohol to bring the solution to the required normality. The solutions of the imido esters were prepared by mixing a standard solution of the imido ester hydrochloride with a sodium ethylate solution of such a concentration that the resulting mixture contained the proper proportions of the two reacting constituents. The sodium

chloride, precipitated out in the above procedure, was allowed to remain in the bottom of the flask, as check experiments with the free benzimido ethyl ester showed that the salt produced no abnormal effect. The titrations were carried out with standard hydrochloric acid and methyl orange but were not very sharp except in the case of the aliphatic imido esters. The aromatic imido ester hydrochlorides are more or less hydrolyzed, while the aliphatic ones, being stronger bases, are much less affected.

In all of the following tables we give the volume of acid necessary to neutralize *both* the ethylate and the imido ester. By subtracting the amount of acid corresponding to the concentration of the ethylate we find the volume of acid necessary to neutralize the imido ester; when this volume is divided by the volume corresponding to a theoretical yield of imido ester (or nitrile) we obtain the "per cent. of imido ester at equilibrium," which is given at the bottom of each table.

Benzonitrile and Benzimido Ethyl Ester

Benzonitrile was purified by redistillation. Its boiling point was constant to within 0°.5, 186°.5–187° (uncorr.).

Benzimido Ethyl Ester Hydrochloride.—This was prepared as described by Pinner,[1] by treating a mixture of one mole benzonitrile and 1.25 moles of alcohol with a little more than 1 mole of dry hydrochloric acid gas. Crystallization was started by adding some of the salt and the solution was allowed to stand at 0° in a well stoppered flask for two or three days, when the solid mass was broken up and washed with cold alcohol and ether. It was preserved in a vacuum desiccator over calcium oxide. It is soluble in alcohol only enough to give a solution a little stronger than half normal.

Benzimido ethyl ester was prepared only in small quantity. The method used was that described by Stieglitz.[2]

To confirm the quantitative data that the addition of alcohol to the benzonitrile takes place as described, a qualitative experiment was carried out as follows: Fifteen grams of benzonitrile dissolved in 75 cc. of alcohol were treated with 25 cc. of a normal solution of sodium ethylate, and the

[1] Die Imidoäther und ihre Derivate, Berlin, **1892**, p. 53.

[2] THIS JOURNAL, **39**, 443.

mixture allowed to stand at 25° for 36 hours. It was then poured into a separating funnel containing 300 cc. of cold water, acidified, and extracted twice with ether. The ethereal solution contained the unchanged nitrile. The aqueous solution was made alkaline and again extracted with ether. The ethereal solution was dried several times over calcium chloride, filtered and treated with dry hydrochloric acid gas. One and three-tenths grams of a white substance were obtained, which resembled in all its properties the benzimido ethyl ester hydrochloride. It melted with decomposition at 124°–126°. The analysis showed that it was probably contaminated with ammonium chloride formed in its isolation.

Analysis: 0.5035 gram gave 0.4602 gram AgCl. Chlorine found, 22.53 per cent.; theoretical for the imido ester salt, 19.11 per cent.; theoretical for ammonium chloride, 66.28 per cent.

The ethereal extract from the acid solution was freed from ether by distillation, and the residue heated to 100° to dry it. Twelve grams of an oil were obtained which was shown by its odor and boiling point, 187°–188°, to be benzonitrile.

Table I.—0.25 N Benzonitrile with Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$[1]	0.75 N		0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		10 cc.		20 cc.	
t	cc. 0.2 N HCl		*t*	cc. 0.1 N HCl	*t*	cc. 0.2 N HCl
0	min.	37.50	0	min. 25.00	0	min. 12.50
5.25	"	38.20	5.66	" 25.36	60	" 13.66
11.5	"	38.44	14	" 25.68	120	" 14.28
20.5	"	38.57	24	" 25.98	210	" 14.65
45	"	38.61	36	" 26.36	22	hrs. 14.88
106	"	38.66	22	hrs. 27.28	26	" 14.85
24	hrs.	38.61	24	" 27.18		
28	"	38.44	144	" 27.12		
48	"	38.35				
72	"	38.38				
Per cent. ester at equil.		9.28		9.12		9.52

[1] *Equal* volumes of the nitrile or imido ester solution and the sodium ethylate were generally used. All the concentrations given in this paper refer to the solutions after mixing.

Table II.—0.25 N Benzimido Ethyl Ester with Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.75 N		0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	50.00	0 min.	25.00	0 min.	18.75
	5 "	43.99	6 "	23.14	20 "	16.69
	15 "	40.70	∞	13.69	45 "	14.10
	25 "	39.21		13.71	89 "	11.35
	40 "	38.70			119 "	10.28
	55 "	38.65			179 "	8.53
	75 "	38.63			239 "	8.25
	∞	38.61			22 hrs.	7.43
					26 "	7.45
Per cent. ester at equil.	8.88		9.60		9.52	

The following table shows the results obtained with varying concentrations of sodium ethylate, the concentrations of the benzonitrile or imido ester being constant:

Table III

Conc. $NaOC_2H_5$	0.25 N benzonitrile Per cent. ester at equil.	0.25 N benzimido ethyl ester Per cent. ester at equil.
0.75 N	9.28	8.88
0.25 N	9.12	9.60
0.125 N	9.52	9.52

The equilibrium point remains constant within the limits of experimental error.

Table IV.—0.5 N Sodium Ethylate with Varying Concentrations of Benzonitrile

Conc. C_6H_5CN	0.5 N		0.5 N	
Vol. taken for each titration	10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	25.00
	20 "	26.34	5 "	25.65
	40 "	26.80	10 "	25.96
	70 "	26.88	15 "	26.19
	∞		25 "	26.57
		26.90	35 "	26.78
		26.89	57	26.86
			∞	26.93
Per cent. ester at equil.	7.60		7.72	

Conc. C_6H_5CN	0.25 N		0.375 N	
Vol. taken for each titration	10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	25.00
	15 "	25.66	7 "	25.58
	44 "	26.02	20 "	26.14
	67 "	26.12	30 "	26.36
	∞	26.11	∞	26.57
Per cent. ester at equil.	9.06		8.37	

Conc. C_6H_5CN	0.125 N		0.0625 N		0.03125 N	
Vol. taken for each titration	20 cc.		20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	50.00	0 min.	50.00	0 min.	50.00
	∞	51.37	∞	50.91	∞	50.47
		51.41		50.90		50.40
		51.40		50.87		50.42
		51.38		50.89		50.46
Per cent. ester at equil.	11.12		14.08$_8$		14.10	

The following table is a collection of the above results, showing the change in the equilibrium point produced by a change in the concentration of the benzonitrile; N sodium ethylate was used in all cases:

Table V

Conc. benzonitrile after mixing	Per cent. imido ester present at equilibrium
0.5 N	7.60
0.5 N	7.72
0.375 N	8.37
0.25 N	9.06
0.125 N	11.12
0.0625 N	14.08
0.03125 N	14.10

The change in concentration of the alcohol due to its combination with the nitrile, and due to the preparation of solutions of different concentrations,[1] is not sufficient to account for this change in equilibrium with change of the concentration of the nitrile; that is, calculations on the basis of a reversible bimolecular-monomolecular reaction give practically the same equilibrium constants as those calculated on the basis of a reversible monomolecular reaction, assuming the concentration of the alcohol to be constant.

p-*Tolunitrile and* p-*Tolimido Ethyl Ester*

The *p*-tolunitrile was purified by extracting with acid, and then with alkali several times. It was then washed thoroughly with water and dried by standing several days in a vacuum desiccator over sulphuric acid. Difficulty is experienced in the titration of solutions containing this nitrile, as it separates out on addition of water, and obscures the color change of the indicator.

p-*Tolimido ethyl ester hydrochloride* was prepared as described by Pinner.[2] The purity of the compound was determined by precipitating the chlorine and weighing the silver chloride.

0.7698 gram substance gave 0.5593 gram AgCl. Theo-

[1] The solutions were prepared on a volume normal basis; therefore, the more concentrated the solution the less alcohol used in preparing it.

[2] *Loc. cit.*, page 61.

retical amount of chlorine, 17.85 per cent.; found, 17.77 per cent.

Table VI.—0.25 N p-*Tolunitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	12.50	0 min.	12.46
	10 "	12.84	∞	14.16
	55 "	13.06		14.14
	115 "	13.18		
	175 "	13.35		
	∞	13.36		
Per cent. ester at equil.	6.80		6.71	

Table VII.—0.25 N p-*Tolimido Ethyl Ester and Sodium Ethylate*

Conc. $NaOC_2H_5$	0.25 N	
Vol. taken for each titration	10 cc.	
	t	cc. 0.2 N HCl
	0 min.	25.00
	10.5 "	22.84
	30.5 "	20.46
	50 "	18.08
	120 "	14.81
	200 "	13.65
	344 "	13.21
	∞	13.27
		13.25
Per cent. ester at equil.	6.08	

m-*Nitrobenzonitrile and* m-*Nitrobenzimido Ethyl Ester* m-*Nitrobenzonitrile.*—This was made by the nitration of benzonitrile with potassium nitrate and sulphuric acid.[1] The crude product obtained was very impure, but was purified by precipitation from hot alcohol by the addition of water. When this process had been repeated three or four times the melting point remained constant at 115°.5–116°. The nitrile

[1] Schöpff: Ber. d. chem. Ges., **18**, 1063.

is not very readily soluble in cold alcohol, the strongest solution which could be obtained at 25° being eighth-normal.

m-*Nitrobenzimido Ethyl Ester Hydrochloride.*—This was prepared as described by Lossen.[1] Ten grams of the nitrile were dissolved in dry benzene, 3.2 grams alcohol added, and 2.46 grams dry hydrochloric acid gas passed in. The solution was allowed to stand for a week, and the precipitate filtered off. Thirteen grams were obtained.

Analysis: 0.7266 gram substance gave 0.4543 gram AgCl. Theoretical amount of chlorine, 15.38 per cent.; found, 15.45 per cent.

Table VIII.—0.0625 N m-*Nitrobenzonitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	50.00	0 min.	25.00
	∞	54.92		29.88
		54.84	∞	30.00
				29.80
Per cent. ester at equil.	78.1		77.7	

Table IX.—0.0625 N m-*Nitrobenzimido Ethyl Ester and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	56.25	0 min.	31.25
	20 "	54.94	35 "	30.08
		54.93		29.76
	∞	54.83	∞	29.80
		54.85		29.83
Per cent. ester at equil.	78.2		76.8	

[1] Ann. Chem. (Liebig), **265**, 144

p-*Nitrobenzonitrile*

(By C. N. Myers)

This substance, which was bought from Hoffman and Kropff, melted at 145°. As the saturated solution at 25° is only 0.084 N, we have used 0.075 N solutions in all of the work. The experiments show that the alcohol and this nitrile react more rapidly than any other aromatic nitrile studied, the equilibrium being attained in about one hour. Portions were tested with *m*-phenylenediamine for sodium nitrite but no great color change was found. This shows that the sodium ethylate does not appreciably remove the nitro group from the benzene nucleus.

Table X.—0.05 N p-*Nitrobenzonitrile and Varying Concentrations of Sodium and Potassium Ethylate*

Conc. ethylate	0.03130 N $NaOC_2H_5$		0.08346 N KOC_2H_5	
Vol. taken for each titration	30 cc.		30 cc.	
	t	cc. 0.1 N HCl	*t*	cc. 0.1 N HCl
	23 min.	17.03	24 min.	33.12
	37 "	17.92	112 "	33.93
	57 "	18.63	187 "	33.97
	74 "	18.63	1260 "	34.30
	1340 "	18.48		
	2778 "	18.38	1300 "	34.28
Per cent. ester at equil.	61.6		61.6	

m-*Bromobenzonitrile and* m-*Bromobenzimido Ethyl Ester*

m-*Bromobenzonitrile* was prepared by Reid's[1] method of distilling the lead salt of *m*-bromobenzoic acid with lead sulphocyanate. It was purified by recrystallization from alcohol and melted at 38°–39°.

m-*Bromobenzimido Ethyl Ester Hydrochloride.*—No description of this compound could be found in the literature, although Stieglitz has used the compound in his investigations on "Catalysis of Imido Ethers."[2] It was prepared as follows: Eight grams of the nitrile were mixed with 2 grams alcohol,

[1] This Journal, **43**, 179.
[2] *Ibid.*, **39**, 609.

and enough dry ether added to bring the nitrile into solution. This was then treated with 1.7 grams dry hydrochloric acid gas, and allowed to stand. The solid which crystallized out was filtered and washed as usual with cold alcohol and ether. Only 2.5 grams were obtained, and no more substance would crystallize out on standing. On evaporation of the ether in a vacuum desiccator, 6.3 grams unchanged nitrile were obtained. This was mixed with 1.6 grams alcohol, and considerable more than the theoretical amount of hydrochloric acid gas passed in.

Three grams of imido ester hydrochloride were obtained.

Analysis: 0.3881 gram substance gave 0.2107 gram AgCl. Theoretical amount of chlorine, 13.40 per cent.; found, 13.42 per cent.

Owing to the difficulty experienced in obtaining this compound in satisfactory yield, it seemed advisable to test whether the reaction of the *m*-bromobenzonitrile, alcohol, and hydrochloric acid is reversible or not. Four-tenths gram portions of this imido ester hydrochloride were weighed out, dissolved in small flasks containing 20 cc. alcohol, and allowed to stand at 25° for different time periods. They were then taken out and titrated with standard sodium hydroxide and methyl orange. Owing to hydrolysis of the *m*-bromobenzimido ethyl ester hydrochloride, the titrations were not at all sharp, and no very definite end point could be determined; so the titrations were carried to approximately the same degree of intensity of the pink color.

Time in days	cc. 0.2 N NaOH
0	0.43
5	0.70
15	0.50
61	0.42

The solutions were then extracted with ether. No *m*-bromo nitrile was detected; its detection, however, would have been made difficult by the ethyl *m*-bromobenzoate formed by the action of the water on the imido ester hydrochloride. We may conclude, therefore, that this reaction, like that of the other ni-

triles with alcohol and hydrochloric acid, is practically non-reversible. That the other imido ester hydrochlorides do not change into nitrile, alcohol and hydrochloric acid was proven by allowing an alcoholic solution of the imido ester hydrochloride to stand. No more alkali was required for neutralization than that used in neutralizing the hydrochloric acid resulting from the hydrolysis of the imido ester hydrochloride.

Table XI.—0.125 N m-*Bromobenzonitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	12.50
	10 "	26.93	40 "	16.77
	31 "	27.25	∞	17.29
		27.35		17.34
	∞	27.37		
		27.37		
Per cent. ester at equil.	37.9		38.5	

Table XII.—0.125 N m-*Bromobenzimido Ethyl Ester and Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N	
Vol. taken for each titration	10 cc.	
	t	cc. 0.2 N HCl
	0 min.	31.25
	13 "	27.44
	52 "	27.40
	170 "	27.32
	∞	27.35
		27.30
Per cent. ester at equil.	37.3	

p-*Bromobenzonitrile*

(By C. N. Myers)

The work with this substance, and with *p*-chlorobenzonitrile, *p*-nitrobenzonitrile, and *o*-bromo-*p*-methylbenzonitrile was done by Dr. C. N. Myers. The *p*-bromobenzonitrile was made by

the Sandmeyer reaction. It melted at 112°.5. The solubility is so small that 0.15 N solutions were used. The imido ester salt is hydrolyzed enough to make the titration somewhat uncertain. Dr. Myers has studied the reaction of 0.15 N *p*-bromobenzonitrile and sodium ethylate whose concentrations varied from N/8 to N/2048. The results show that the ethylate ions and the nonionized sodium ethylate are about equally effective in catalyzing the reaction. In calculating the reaction velocities, he used the formula

$$\frac{dx}{dt} = K_1 (A_1 - x) - K_2 x$$

or

$$K_v = K_1 + K_2 = \frac{KA_1}{KA_1 - (K+1)x}$$

in which A_1 is the original concentration of the nitrile, and x the concentration of the imido ester formed during the reaction. At equilibrium we have

$$K = \frac{K_1}{K_2} = \frac{x}{A_1 - x}$$

Table XIII.—0.15 N p-*Bromobenzonitrile and 0.00781 N Sodium Ethylate*

Ten cc. taken for each titration

A_1 = 30 cc.			K = 0.373		
t	x^1	K_v	t	x^1	K_v
72 min.	1.53	0.00124	48 min.	1.05	0.00125
102 "	2.07	0.00125	58 "	1.24	0.00124
134 "	2.62	0.00126	99 "	2.04	0.00126
174 "	3.28	0.00129	118 "	2.36	0.00126
259 "	4.26	0.00121	170 "	3.14	0.00124
277 "	4.43	0.00123	233 "	3.89	0.00121
312 "	4.72	0.00121			
	Ave.,	0.00124		Ave.,	0.00124
Per cent. ester at equil.		27.17			27.17

[1] See footnote p. 145.

Table XIV.—0.15 N p-*Bromobenzonitrile and 0.0039 N Sodium Ethylate*

Ten cc. taken for each titration

A_1 = 30 cc. K = 0.373

t	x[1]	K_v	t	x[1]	K_v
92 min.	1.04	0.000644	104 min.	1.14	0.000629
150 "	1.62	0.000638	128 "	1.39	0.000634
231 "	2.37	0.000646	178 "	1.86	0.000632
290 "	2.81	0.000633	208 "	2.12	0.000629
326 "	3 14	0.000648	312 "	3.01	0.000640
			377 "	3.45	0.000634
	Ave.,	0.000642		Ave.,	0.000633

Per cent. ester at equil. 27.17 27.17

p-*Chlorobenzonitrile*

(By C. N. Myers)

This compound was bought from Hoffman and Kropff. It melted at 92°.

Table XV.—0.1 N p-*Chlorobenzonitrile and 0.06255 N Sodium Ethylate*

Conc. $NaOC_2H_5$ 0.06255 N

Vol. taken for each titration 10 cc.

t	cc. 0.1 N HCl
249 min.	17.36
1010 "	17.42
1347 "	17.64
2495 "	17.65
3995 "	17.67

Per cent. ester at equil. 25.85

o-*Bromo*-p-*methylbenzonitrile*

(By C. N. Myers)

We have carried out a few experiments with this substance and with *o*-tolunitrile to learn whether the so-called space interference prevents the reaction of these nitriles with the alcohol. As was predicted, the reaction is so slow that practically no imido ester is formed even in five months.

[1] In these four tables we have called x the number of cc. of 0.1 N hydrochloric acid required to neutralize the imido ester formed.

Table XVI.—0.25 N o-Bromo-p-methylbenzonitrile and 0.25 N Sodium Ethylate

t	Cc. 0.1 N acid	Original titration	Cc. change
30 min.	25.00	25.02	—0.02
1400 "	25.02	25.03	—0.01
150 days	24.70	25.00	—0.30
150 "	24.74	25.00	—0.26

No precipitate was obtained when silver nitrate was added. Nitric acid was used in these titrations. Check experiments on the ethylate solutions show that small disturbing side reactions take place which, however, do not change the conclusion that the nitrile hardly reacts with the alcohol

Acetonitrile and Acetimido Ethyl Ester

Acetonitrile was purified by repeated distillation over phosphorus pentoxide and then alone.

Acetimido Ethyl Ester Hydrochloride.—Owing to the much greater reactivity of the aliphatic imid. ester hydrochlorides with alcohol to form ortho esters and ammonium chloride, and with water to form ethyl acetate and ammonium chloride, their preparation is usually accompanied with the formation of more or less ammonium chloride. If, according to the method described by Pinner,[1] the mixture of nitrile, alcohol and hydrochloric acid is allowed to stand until the hydrochloride crystallizes out, a pure preparation cannot be obtained; it is contaminated with more or less ammonium chloride. The following procedure gives a quantitative yield of very pure substance: Fifteen grams of acetonitrile and 17 grams alcohol cooled with ice were treated with 13 grams of dry hydrochloric acid gas. The sides of the flask were rubbed with a glass rod to induce crystallization from the viscous mass. After standing in the cold for 5 hours the whole contents of the flask had solidified to a hard crystalline mass which often could be removed only by breaking the flask. The mixture was allowed to stand packed in ice overnight (about

[1] *Loc. cit.*, page 27.

14 hours),[1] and was taken out, powdered, and washed 2 or 3 times with dry ether. Yield, 45 grams (theoretical yield, 45.2 grams).

Analysis: 0.9724 gram of substance gave 1.1302 gram AgCl. Chlorine: found, 28.76 per cent.; theoretical, 28.69 per cent.

The rapid decomposition of the imido ester hydrochloride into ammonium chloride in the course of the usual method of preparation is shown in the following experiment: Fifteen grams of acetonitrile, 17 grams alcohol, and 13 grams dry hydrochloric acid were allowed to stand overnight packed in ice. In the morning, on rubbing the sides of the flask, some of the substance crystallized out. This was filtered off immediately and washed with dry ether; yield, 23 grams (Sample *A*). The filtrate and washings were allowed to stand overnight and the precipitate filtered off; yield, 13.5 grams (Sample *B*). The filtrate from this was allowed to stand for four days and then the precipitate filtered off; yield, 3 grams (Sample *C*). From this filtrate, a week later, a fourth fraction was obtained (Sample *D*), 0.4 gram. Each sample was dried in a vacuum desiccator over burnt lime before analysis.

Analysis of Sample *A*:

1.1135 grams substance gave 1.2954 grams AgCl. Found chlorine, 28.77 per cent. 0.2000 gram substance required 16.23 cc. 0.1 N $AgNO_3$. Found chlorine, 28.77 per cent. 0.3662 gram required 29.82 cc. 0.1 N $AgNO_3$. Found chlorine, 28.87 per cent. Theoretical chlorine, 28.69 per cent.

Analysis of Sample *B*:

0.5804 gram substance required 49.91 cc. 0.1 N $AgNO_3$; found chlorine, 30.41 per cent.

0.4120 gram substance required 35.36 cc. 0.1 N $AgNO_3$; found chlorine, 30.43 per cent.

Analysis of Sample *C*:

0.1778 gram substance required 32.82 cc. 0.1 N $AgNO_3$; found chlorine, 65.47 per cent.

Analysis of Sample *D*:

[1] In later experiments, crystals of the pure acetimidoethyl ester hydrochloride were added after the mixture had stood in ice a couple of hours. In the morning the whole contents of the flask had crystallized out in characteristic large crystals, and could be filtered off immediately.

0.3656 gram substance required 67.71 cc. 0.1 N $AgNO_3$; found chlorine, 65.68 per cent. Theoretical chlorine for NH_4Cl, 66.28 per cent.

The fact that the samples, when dissolved in water, did not give any acidity, and that after standing one or two days in a vacuum desiccator over burnt lime, the chlorine content did not change, shows that there was no free hydrochloric acid occluded in the precipitate.

That the pure acetimido ethyl ester hydrochloride can be kept without appreciable decomposition is shown by the following data:

1. Analysis of a sample gave 28.76 per cent. chlorine. Same sample 20 days later gave 28.76 per cent. chlorine.

2. Analysis of a sample gave 28.77 per cent. chlorine. Same sample 6 days later gave 28.80 per cent. chlorine.

Decomposition of the Acetimido Ethyl Ester Hydrochloride into Acetamide and Ethyl Chloride

This decomposition, which takes place very rapidly when the substance is heated to its melting point, was found to take place slowly in alcoholic solution at 25°. Weighed amounts of the imido ester hydrochloride were dissolved in small flasks in 20 cc. alcohol and allowed to stand at 25° for different time periods. They were then taken out, poured into water, and the chlorine determined. Ammonium chloride crystallized out in the flasks, owing to the reaction between the imido ester hydrochloride and alcohol to form ortho ester and ammonium chloride. The following table shows the gradual loss of chlorine due to the above decomposition and escape of ethyl chloride:

Time (hours)	Wt. hydrochloride taken	Wt. AgCl obtained	Per cent. chlorine
0.50	1.1251	1.3040	28.67
2.50	1.2080	1.3948	28.56
48.0	1.2914	1.4793	28.33
150.0	1.2355	1.3822	27.73

The acetimido ester hydrochloride used in the above experiments contained 28.76 per cent. chlorine. The acetamide was not isolated.

Table XVII.—0.25 N Acetonitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	10 cc.		20 cc.	
t	cc. 0.2 N HCl		*t*	cc. 0.2 N HCl
0 min.	25.00		0 min.	25.00
5 "	25.20			
37 "	25.21		∞	25.46
∞	25.20			25.44
	25.22			
Per cent. ester at equil.	1.68			1.80

Conc. $NaOC_2H_5$	0.125 N		0.0625 N	
Vol. taken for each titration	20 cc.		20 cc.	
t	cc. 0.2 N HCl.		*t*	cc. 0.2 N HCl
0 min.	12.50		0 min.	6.25
∞	12.92		∞	6.64
	12.90			6.65
				6.65
Per cent. ester at equil.	1.64			1.80

Table XVIII.—Varying Concentrations of Acetonitrile and Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N	0.25 N	0.25 N
Conc. nitrile	0.5 N	0.125 N	0.0625 N
Vol. taken for each titration	10 cc.	20 cc.	20 cc.
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	25.00	0 min.	24.68	0 min.	24.97
∞	25.36	∞	24.98	∞	25.12
	25.35		25.00		25.14
	25.35				25.13
	25.38				
Per cent. ester at equil.	1.44		2.48		2.56

Table XIX.—0.25 N Acetonitrile and Varying Concentrations of Potassium Ethylate

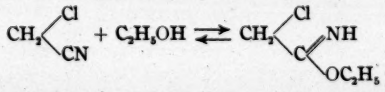
Conc. KOC_2H_5	0.5 N		0.25 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.05	0 min.	25.06
	∞	25.22	∞	25.53
		25.24		25.54
Per cent. ester at equil.		1.44		1.88

Conc. KOC_2H_5	0.125 N		0.0625 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	12.48	0 min.	6.28
	10 "	12.58	10 "	6.34
	60 "	12.70	∞	6.62
	∞	12.86		6.64
		12.84		6.65
Per cent. ester at equil.		1.48		1.44

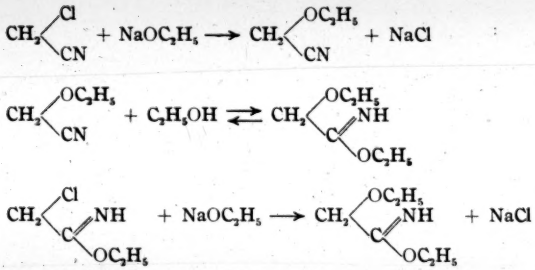
Chloroacetonitrile

Chloroacetonitrile was made as described by Bisschopinck.[1] It was redistilled several times over phosphorus pentoxide and then alone.

The action of sodium ethylate on the chloroacetonitrile does not consist in the simple addition of alcohol with formation of the imido ester. The sodium ethylate, besides acting as catalyst, replaces the chlorine by an ethoxy group with formation of sodium chloride, which after sufficient time precipitates. The following reactions probably take place:



[1] Ber. d. chem. Ges., **6**, 732. Bauer: Ann. Chem. (Liebig), **229**, 167. Scholl and Steinkopf: Ber. d. chem. Ges., **39**, 2417; **41**, 2540. Acree and Loy: THIS JOURNAL, **45**, 227.



The data obtained show that the equilibrium point is widely different from that of the other aliphatic nitriles studied. The alkalinity of a mixture of sodium ethylate and chloroacetonitrile first increases with time and then begins to decrease.

Table XX.—0.25 N Chloroacetonitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.25 N		0.0625 N	
Vol. taken for each titration	10 cc.		10 cc.[1]	
t	cc. 0.2 N HCl	*t*	cc. 0.2014 N HNO_3	cc. 0.1 N $AgNO_3$
0 min.	12.50	0 min.	3.10	0.00
9 "	23.06	5 "	14.66	0.50
20 "	23.36	18 "	14.64	0.39
29 "	23.68	38 "	14.60	0.65
47 "	23.46	67 "	14.35	0.82
77 "	23.25	156 "	14.25	0.90
19 hrs.	18.25	178 "	14.08	1.10
24 "	17.48	27 hrs.	12.61	1.34[2]
48 "	13.49			
Per cent. ester[3] at equil.	81.0		94.0	

[1] The solutions were first titrated with nitric acid to neutrality, then the chlorine determined with silver nitrate and potassium chromate.

[2] Sodium chloride had precipitated.

[3] The equilibrium points are not accurate, owing to the complications of the reactions, but the data show that the equilibrium is markedly different from that of the other aliphatic nitriles studied.

Propionitrile and Propimido Ethyl Ester

The propionitrile was obtained from Kahlbaum, and was purified by distilling twice over a little phosphorus pentoxide, and then alone.

Propimido ethyl ester hydrochloride was prepared by treating a mixture of nitrile and alcohol cooled with ice with dry hydrochloric acid gas as described by Pinner.[1] This was allowed to stand overnight in ice, and then the oily mass of crystals filtered and washed with dry ether (Sample *A*). The filtrate was allowed to stand a day longer when more crystals were obtained (Sample *B*).

Analysis of Sample *A*:

0.1587 gram required 11.86 cc. 0.1 N $AgNO_3$. Found chlorine, 26.50 per cent.; theoretical, 25.78 per cent.

Analysis of Sample *B*:

0.1491 gram required 11.34 cc. 0.1 N $AgNO_3$. Found chlorine, 26.96 per cent.

Table XXI.—0.25 N Propionitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N	0.125 N
Vol. taken for each titration	10 cc.	20 cc.
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	25.00	0 min.	12.50
3 "	25.05		
10 "	25.09	∞	12.97
39 "	25.21		12.92
	25.22		
∞	25.22		
	25.21		
Per cent. ester at equil.	1.76		1.76

[1] *Loc. cit.*, page 28.

Table XXII.—0.25 N Propimido Ethyl Ester and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
t	cc. 0.2 N HCl		*t*	cc. 0.2 N HCl
0 min.	37.50		0 min.	37.50
5 "	33.37		5 "	35.13
20 "	27.96		25 "	29.29
31 "	26.73			
46 "	25.86		∞	14.36
62 "	25.75			14.32
	25.56	[1]		
∞	25.58			
	25.56			

Butyronitrile

Butyronitrile was obtained from Kahlbaum and was purified by distillation, first over phosphorus pentoxide and then alone.

Table XXIII.—0.25 N Butyronitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.		20 cc.	
t	cc. 0.2 N HCl		*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	25.00		0 min.	25.03	0 min.	12.46
5 "	25.01		∞	25.26	∞	12.69
25 "	25.04			25.28		12.71
52 "	25.07					
	25.10					
∞	25.13					
	25.12					
	25.11					
Per cent. ester at equil.	0.89		0.96		0.96	

[1] The equilibrium point could not be determined accurately to compare with that obtained by starting with the nitrile, owing to the decomposition of the imido ester hydrochloride into ammonium chloride in the time required to prepare the solutions, and also to a contamination of the imido ester hydrochloride with ammonium chloride.

The imido ester from this nitrile was not prepared, as, from the description of it by Pinner,[1] it was deemed too unstable to work with.

Diisoamylcyanoamide and Ethyl Diisoamylisourea

Diisoamylcyanoamide and Sodium Ethylate.—The diisoamylcyanoamide was prepared as described by McKee.[2] It was purified by redistillation *in vacuo*. The ethyl diisoamylisourea was prepared from the cyanoamide and sodium ethylate according to McKee's[3] directions, and was purified by fractionation *in vacuo*. The reaction between the cyanoamide and alcohol in the presence of sodium ethylate goes very slowly at 25°. Attempts to follow the reaction by the titration of the isourea formed give only approximate figures as the cyanoamide itself titrates slightly with hydrochloric acid, and makes the end point very uncertain.

Table XXIV.—0.25 N Diisoamylcyanoamide and 0.25 N Sodium Ethylate

At 25°[4]		At 100°[5]	
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	12.49	0 hrs.	12.48
3 "	12.56	1 "	23.10
30 "	12.66	2 "	23.30
75 "	12.80	4 "	23.80
17 hrs.	14.02	7 "	24.30
21 "	14.38	11 "	24.40
25 "	14.62	95.36 per cent. isourea formed.	
120 "	19.34		
10 days	23.10		

Ten cc. of the above mixture was allowed to stand at 25° for *ten* days. It required 23.1 cc. 0.2 N hydrochloric acid

[1] *Loc. cit.*, page 30.
[2] THIS JOURNAL, **38**, 208.
[3] *Ibid.*, **42**, 1.
[4] Ten cc. taken for each titration.
[5] Fifty cc. portions of the two solutions were mixed and 10 cc. portions placed in small tubes, sealed, and heated for the required time in a boiling water bath, and then titrated. Probably equilibrium had not been attained in these experiments.

for neutralization. Therefore, the reaction goes as far in one hour at 100° as in ten days at 25°.

Ethyl Diisoamylisourea and Sodium Ethylate.—The purity of the isourea was tested as follows: 0.5785 gram was poured into water and titrated with 0.2 N hydrochloric acid, using methyl orange as indicator. Required, 12.73 cc.; theoretical, 12.67 cc.

Table XXV.—0.25 N Diisoamylisourea and 0.25 N Sodium Ethylate[1]

t	cc. 0.2 N HCl
0 hours	25.31
0.5 "	25.25
1 "	25.00
3 "	24.94
5 "	24.96
9 "	24.99

2.08 per cent. cyanoamide formed

In this case (also chloracetonitrile) we have a reaction which goes almost to completion to form the isourea (corresponding to the imido ester); while in the case of the acetonitrile, propionitrile and butyronitrile, the reaction proceeds almost entirely in the other direction, to form the nitrile from the imido ester. The other nitriles studied show intermediate values of the equilibrium point.

[1] Equal amounts of the two solutions were mixed and 10 cc. portions placed in small tubes, sealed, and heated for different time periods at 100°, and then titrated.

Table XXVI.—Nitriles, or Imido Esters, and Sodium Ethylate in Absolute Ethyl Alcohol at 25°

Nitrile	Conc. of nitrile or imido ester at beginning	Conc. of sodium ethylate	Per cent. imido ester at equilibrium from nitrile side	Per cent. imido ester at equilibrium from imido ester side
Benzonitrile	0.500 N	0.500 N	7.60	....
"	0.375 N	0.500 N	8.37	....
"	0.250 N	0.75 N	9.28	8.88
"	0.250 N	0.25 N	9.12	9.60
"	0.250 N	0.125 N	9.52	9.52
"	0.125 N	0.500 N	11.12	....
"	0.0625 N	0.500 N	14.08	....
	0.03125 N	0.500 N	14.10	....
p-Tolunitrile	0.250 N	0.250 N	6.80	6.08
"	0.250 N	0.250 N	6.71	....
m-Nitrobenzonitrile	0.0625 N	0.500 N	78.1	78.2
"	0.0625 N	0.250 N	77.7	76.8
p-Nitrobenzonitrile	0.05 N	0.0313 N	61.6	....
"	0.05 N	0.08346 N (KOC_2H_5)	61.6	....
m-Bromobenzonitrile	0.125 N	0.500 N	37.9	37.3
"	0.125 N	0.125 N	38.5	....
p-Bromobenzonitrile	0.15 N	0.00781 N	27.17	....
"	0.15 N	0.0039 N	27.17	....

p-Chlorobenzonitrile	0.10	N	0.0625	N		25.85	....
Acetonitrile	0.500	N	0.500	N		1.44	....
"	0.250	N	0.500	N		1.68	....
"	0.250	N	0.500	N	(KOC_2H_5)	1.44	....
"	0.250	N	0.250	N		1.80	....
"	0.250	N	0.250	N	(KOC_2H_5)	1.88	....
"	0.250	N	0.125	N		1.64	....
"	0.250	N	0.125	N	(KOC_2H_5)	1.48	....
"	0.250	N	0.0625	N		1.80	....
"	0.250	N	0.0625	N	(KOC_2H_5)	1.44	....
"	0.125	N	0.250	N		2.48	....
"	0.0625	N	0.250	N		2.56	....
Chloroacetonitrile	0.25	N	0.25	N		81.00	(?)....
"	0.25	N	0.0625	N		94.00	(?)....
Propionitrile	0.250	N	0.500	N		1.76	....
"	0.250	N	0.125	N		1.76	....
Butyronitrile	0.250	N	0.500	N		0.89	....
"	0.250	N	0.250	N		0.96	....
"	0.250	N	0.125	N		0.96	....
Diisoamylcyanoamide at 100°	0.250	N	0.250	N		95.36	2.08

It is evident then that the equilibrium point varies very widely when we start with different nitriles in different concentrations, the amount of imido ester left at equilibrium being represented by 1, 1.75, 6.8, 9.2, 14.1, 25.85, 27.17, 38.5, 61.6, 78, and 95 per cent. for different compounds.

CONCLUSIONS

(1) The experimental work shows that nitriles add ethyl alcohol reversibly in the presence of sodium, potassium and lithium ethylates. The per cent. of imido ester present when equilibrium is attained is practically the same whether we start with the nitrile or the imido ester. The equilibrium point varies very widely with the different nitriles.

(2) A few experiments given in this article and other unpublished work show that the reaction velocity can be expressed as a function of the concentration of *both* the ethylate ions and the nonionized ethylate salts.

JOHNS HOPKINS UNIVERSITY
December 1, 1912

REPORT

A CHEMICALLY ACTIVE MODIFICATION OF NITROGEN

It has been frequently observed that vacuum tubes, subjected to an electric discharge, show a luminosity of the contained gas after the discharge is over. If the tube contains carefully purified nitrogen there is no appreciable afterglow when the ordinary discharge is used, but with the jar discharge there is a distinct yellow glow after the discharge is stopped, the glow gradually fading and disappearing completely after about one minute.

This glowing nitrogen has some very remarkable properties which have recently been made the subject of an extended study by Strutt and Fowler.[1]

The glow gives a characteristic band spectrum, otherwise unknown, the most conspicuous bands being green, yellow and red, of approximately the same intensity. The spectrum is similar to the ordinary nitrogen spectrum obtained by using the uncondensed discharge, but is not identical with it. Many

[1] Strutt: P. Roy. Soc., [A] **85**, 219. Fowler and Strutt: *Ibid.*, **85**, 377. Strutt: *Ibid.*, **86**, 56. Strutt and Fowler: *Ibid.*, **86**, 105. Strutt: *Ibid.*, **86**, 262. Strutt: *Ibid.*, **87**, 179.

of the nitrogen bands are wanting and there are certain bands not present in the nitrogen spectrum. The experiments carried out seem to point to the view that, under the influence of the discharge, ordinary nitrogen is converted into an allotropic modification, probably monatomic, which reverts rapidly to ordinary nitrogen. The glow is regarded as a phenomenon accompanying this reversion to the ordinary form.

Chemical Properties

Glowing nitrogen possesses remarkable chemical properties. When it is drawn through a tube containing a pellet of yellow phosphorus a violent reaction occurs, the glow is destroyed, red phosphorus is formed and nitrogen is absorbed. In contact with iodine vapor at the ordinary temperature, a "magnificent light blue flame" is produced. A reaction also takes place when sulphur and aersnic are gently heated in the glowing gas. Selenium, carbon, antimony and hydrogen are without effect. When oxygen is admitted the glow is quickly destroyed, but no combination takes place. The oxygen appears to destroy the glow catalytically. If there is any trace of oxygen in the nitrogen that is led into the discharge tube, no afterglow is produced. When metallic sodium is heated a little above its melting point in contact with the glowing nitrogen, the complete sodium spectrum is developed and nitrogen is absorbed. When the metal is heated to 250° the yellow line *D* becomes almost invisible and the green line *E* shows up strongly. There is also a reaction with mercury vapor, forming an explosive compound and developing the mercury spectrum.

Of particular interest is the reaction with nitric oxide. When this gas is mixed with glowing nitrogen, a brilliant flame is produced and nitrogen peroxide is formed. The reaction is represented thus: $2NO + N \longrightarrow NO_2 + N_2$. Advantage is taken of this reaction to determine the percentage of active nitrogen formed in the discharge tube. An excess of nitric oxide is mixed with the glowing nitrogen immediately after it leaves the discharge tube and the mixture of gases led through a U-tube cooled by liquid air. At the low temperature nitrogen peroxide combines with more nitric oxide to form the trioxide, which condenses to a blue liquid. From the weight of nitrogen trioxide formed the percentage of active nitrogen is calculated. The maximum amount obtained is 2.46 per cent.

Active nitrogen reacts with acetylene, forming cyanogen, and with a large number of organic compounds containing

halogens, forming in every case cyanogen and liberating the halogen.

Certain substances, notably copper oxide and manganese dioxide, destroy the glow very quickly, without themselves undergoing any change, apparently. The reaction is regarded as catalytic.

Effect of Temperature

When a stream of glowing nitrogen is drawn slowly through a tube cooled by liquid air, the glow is greatly increased in brilliancy and dies out completely before the coldest part of the tube is reached. When the gas is drawn through a tube moderately heated in one part, the glow is locally extinguished, but reappears farther along the tube. From these experiments it appears that the rate of transformation of active into ordinary nitrogen, of which the intensity of the glow is regarded as an index, is accelerated by lowering and retarded by raising the temperature. The experiments are, however, not conclusive, because of changes in density, which, independently of temperature changes, affect the rate of transformation. Density changes may be avoided by employing sealed bulbs containing glowing nitrogen. Under these conditions the glow is much brighter and of shorter duration when the bulb is immersed in liquid air than when maintained at room temperature. When a similar bulb is immersed in boiling water the life of the glow is again somewhat shortened, though less than before, and the intensity of the glow is very much less.

Still the phenomena are somewhat complicated. There are here two factors affecting the rate of transformation. One is the direct temperature effect, the other is the catalytic effect of the walls of the vessel, also variable with the temperature. Conclusive experimental evidence is adduced to show that the walls of the containing vessel exert a catalytic action and it seems very probable that this effect increases with rise in temperature, as with copper oxide. Strutt concludes that, were it not for the increased catalytic action of the glass walls at the higher temperature, the duration of the glow would be increased in proportion to the diminution of the intensity and points out that we have here a chemical reaction, viz., the transformation of active into ordinary nitrogen, which is entirely unique in that the velocity is accelerated by lowering and retarded by raising the temperature.

Effect of Density

When active nitrogen is compressed, the glow increases in brilliancy and when the gas is restored to its original volume

the glow is less intense than it would have been after the same time interval without compression. Increase of concentration, therefore, not only increases the luminosity, as might have been predicted since the luminosity depends on the amount of transformation per unit volume, but also increases the total change. From this Strutt concludes that the reaction must be other than monomolecular. The evidence here, however, as described, does not seem entirely conclusive, as Strutt appears to have neglected to take into account the increased catalytic action of the walls of the vessel at the higher concentration. It seems obvious that, admitting a catalytic action of the glass, the effect of this action would be greater the more concentrated the gas. The conclusion, however, is not necessarily vitiated by this apparent omission.

Ionization Attendant on Active Nitrogen

When two electrodes, with a difference of potential of two volts, are introduced into glowing nitrogen the amount of current that passes is great enough to be detected by means of an ordinary galvanometer. The ionization is approximately equal to that of a salted Bunsen flame. Rough quantitative measurements show that, assuming that each ionized molecule of active nitrogen furnishes one positive and one negative ion, one out of every fifteen hundred molecules is ionized. This small degree of ionization, as compared with the total quantity of active nitrogen present, leads to the conclusion that the chemical properties of glowing nitrogen are due to the presence of a definite chemical substance and not to some unexplained survival of the conditions of the discharge, and that the formation of ions is a secondary phenomenon associated with active nitrogen or produced by its reversion to the ordinary form. This view is in harmony with the fact that, when the glowing gas is subjected to the influence of an electric field strong enough to remove any ions that may have resulted directly from the discharge, the intensity of the glow is not diminished.

Strutt is led to the same conclusion in regard to the presence in glowing nitrogen of a definite chemical substance by a study of the energy changes accompanying the disappearance of the glow. He finds that when the glow is destroyed by contact with copper oxide, the amount of heat liberated is comparable with that evolved in other gaseous reactions.

Spectra Produced by Active Nitrogen

As already pointed out, glowing or "active" nitrogen reacts readily with a large number of elementary and com-

pound substances, in some instances at room temperature and in others at moderately elevated temperatures, striking luminosity effects being produced in many cases. In general, the spectra developed are not very different from those obtained by other methods, but in some cases additional lines are shown, especially in the more refrangible parts of the spectrum. Thus the spectra of iodine, tin chloride, mercuric iodide, cuprous chloride and cyanogen are more completely developed than by other means. Sulphur gives a series of bands which are quite distinct from those given by sulphur in a vacuum tube.

From a study of the reactions of active nitrogen, Strutt is led to some interesting speculations concerning reactions in general. Apparently no direct observations of volume changes during transformation have been made and the determination of the ratio of specific heats of active nitrogen probably presents insuperable difficulties. It therefore cannot be said positively that this substance is monatomic, but its reactions in general are best explained on the assumption of the monatomic molecule. Making this assumption, the transformation of active into ordinary nitrogen appears to be unique in two particulars: 1. It is the only reaction studied in which both reacting substances are monatomic, that is, two monatomic molecules react, nonreversibly, to form a diatomic molecule, and 2. It is the only known reaction the velocity of which has a negative temperature coefficient. It is suggested that this is not accidental but that the two are causally related.

The kinetic theory requires that when heat is added to a gas consisting of polyatomic molecules the added energy goes partly to increase the translational velocity of the molecules and partly to increase the internal motion of the molecules, and that in monatomic gases the entire heat energy added appears in increased translational velocity. It is usually assumed that raising the temperature increases the velocity of reaction by increasing the frequency and violence of collisions. Now assuming active nitrogen to be monatomic, its transformation to ordinary nitrogen is a reaction which we might expect to have a greater temperature coefficient of velocity than is usually the case. But, on the contrary, we find a negative effect. The conclusion that increase of translational velocity, in itself, is a hindrance to reaction is obvious. "If we permit ourselves the analogy of India rubber balls coated with some adhesive substance, the more violent the collision, the less likely it is that the balls will permanently adhere."

It is suggested that for reactions in general in which polyatomic molecules are involved, the increase in translational velocity due to rise in temperature exerts also a positive hindrance, but the simultaneous increase in internal energy more than balances the unfavorable influence of greater translational velocity and, upon the whole, a rapid increase in the rate of combination takes place. B. F. LOVELACE

REVIEWS

DER ENERGETISCHE IMPERATIV. Von WILHELM OSTWALD. Erste Reihe. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. s. 544. Preis: brosch., M. 9.60; geb., M. 10.60.

Under this strange title the author has brought together some fifty short papers covering an extraordinary range of subjects—the peace movement, the reform of the calendar, Sir William Ramsay, the proposed Hamburg University, the philosophy of nature, Esperanto, *auch alle Dinge überhaupt*. The volume exemplifies more than any previous one the amazing abundance and the highly scattering character of Ostwald's present literary production. But in the author's eye this miscellany is a unity, because most of its parts exhibit different aspects of a single idea. The book sets forth the ethics—theoretical and applied—of a physical chemist—an ethics (ostensibly) deduced entirely from the second law of thermodynamics. The *Dissipationsgesetz* is the "universal source of all values" (59); not merely the chief, but the only, end of man, is to delay the increase of the entropy (in Clausius' sense) of the universe. The "energetical imperative" therefore runs: "Thou shalt not squander energy, but utilize it!" The chief practical inferences here drawn from this principle appear to be that one ought to join the *Monistenbund* (13) and also the movement known as *Die Brücke*, for introducing economic methods into intellectual work, primarily by standardizing the *formats* of books and paper (15); that we need an artificial universal language; that wars and standing armies are bad things; and that the fatigue-factor in education should be taken account of by teachers.

For the knowledge of these practical truths (except the first, mankind luckily did not have to wait for the discovery of energetics. It is true that, down to the end of the 18th century, people in general had no clear and vivid sense of the quantitative limitation of the world's usable resources, and consequently no *generalized* apprehension of the problem of conservation. To a sharp practical realization of the fact

of limitation men were first brought by economics (Malthus); next by the Darwinian biology. Of this fact the principle of Clausius undoubtedly gives the final and most striking generalization; and it therefore lends to that important moral discovery of the 19th century—the duty of systematic conservation—a certain additional impressiveness. This Ostwald does well to bring out. But the applications which seem to interest him most are in large part either the most trivial or the most debatable phases of energy-conservation; he makes no attempt to draw out methodically and evaluate judiciously the many possible applications of his "imperative;" and of many important ones he shows little appreciation. As a systematic ethical theory his reasonings scarcely merit discussion. It is obvious that the rational ends of human choice are not *determined* by the law of the degradation of energy. That law merely formulates one of the important conditions of their realization. Energy is worth conserving only because there are concrete human values to which its utilization is contributory. And the conversion of free energy into mechanical work is not good in itself, but only if the work satisfies some desire, or leaves some one free for qualitatively more valuable modes of conscious life.

Chemists will perhaps be especially interested in the pleasantly written sketches of the characters and work of eminent men of science—Pierre Curie, van't Hoff, Abbé, Ramsay—with which the volume concludes; and in the book as a whole as a self-revelation of the ardent, generous and "temperamental" personality of a great chemist—who cannot unqualifiedly be called a great moral philosopher. A. O. LOVEJOY

PHOTOCHEMISCHE VERSUCHSTECHNIK. Von DR. PHIL. ET MAG. CHEM. JOHANNES PLOTNIKOW, Privatdozent der Chemie an der Kaiserlichen Universität zu Moskau. Mit 189 Figuren, 50 Tabellen und 3 Tafeln. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. xv + 371. Price, M. 11.00.

This is a very useful reference book for those engaged upon photochemical investigations. Part I deals with the lamps of various types which are used in the study of the action of light upon chemical compounds. The mercury arc in its various forms is very fully described, including the recently perfected quartz lamps which were first brought out by Heraeus of Hanau. These lamps are extremely useful in all photochemical work, on account of their powerful ultraviolet radiation. They are now manufactured (in a greatly improved form) in this country by the Cooper-Hewitt Co., of Hoboken, N. J., and so far as the experience of the reviewer goes, are far superior

to the German lamps, both in point of durability and intensity. Various other sources of light are next dealt with, such as metallic and carbon arcs, condenser sparks, colored flames, Nernst lamps and X-ray tubes, with considerable data relating to ray filters.

In Part II the author devotes considerable space to light thermostats for investigating photochemical reactions at constant temperature, closing with a brief treatment of methods of making organic preparations which, on account of the sensitiveness to light of the products formed, have to be carried out in total darkness, or in retorts and condensers of deep red glass.

Part III deals with optical measuring instruments, photometry, radiation laws, sensitiveness of the eye, absorption and refraction measurements, and rotation of the plane of polarization.

Lecture experiments are taken up in Part IV, dealing with the following subjects: Laws of photochemical reactions, accelerating action of light, photochemical equilibrium, decomposition of organic compounds by ultraviolet light, and selective absorption; then follows a chapter on fluorescence, phosphorescence and triboluminescence, and a chapter on photoelectric phenomena.

The author is not always particular about his references as, for example, on page 233 he describes Wood's experiments on the fluorescence of iodine and bromine without making any reference at all, and the ultraviolet ray filter of nitrosodimethylaniline, in combination with blue glass or copper sulphate, described by Wood over ten years ago, which he attributes to H. Lehmann. Lehmann's only contribution was the substitution of Zeiss's modern blue uviol glass for the cobalt glass used in the earlier experiment. His references are given at the end of each chapter, and, though very numerous, are nearly useless, as the subject of the paper is never given, and there is no way of connecting any given matter in the text with its reference. The last quarter of the book is made up of very useful tables of the temperature coefficients of photochemical reactions, spectra of the elements, and the values of λ, $1/\lambda$ and $N = c/\lambda \cdot 10^{12}$ for values of λ from 2000 to 8000 Ångström units, and the functions l^{-x} and $\tan^2 \alpha$.

As the title indicates, the book deals largely with methods of investigation and manipulation, and as such can be recommended as a reference book. R. W. W.

OXIDATIONS AND REDUCTIONS IN THE ANIMAL BODY. By H. D. DAKIN, D.Sc., F.I.C., The Herter Laboratory, New York. Monographs on Biochemistry, Edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 135. Price, $1.40.

This monograph is an orderly arrangement of a large amount of important but somewhat disconnected material concerning animal metabolism, supplemented, where a logical demand occurs, by results of original investigation. From a long and intimate acquaintance with the subjects discussed, the author has acquired certain definite ideas of animal metabolism and he proceeds to show that these ideas follow of necessity from the facts of the case. Ample opportunity, however, is given to those who are disposed to differ from him and the best arguments for refuting his theory are always furnished. On page 64 we read: "*The writer is of the opinion that the path of phenylalanine and tyrosine katabolism does not lie by way of homogentisic acid.*" But the writer frankly adds: "*The opposite view is, however, very commonly held,*" and proceeds to show how a benzene derivative with a hydroxyl group substituting position *three* may give rise in the organism to a compound in which the substituting hydroxyl group occupies position *four*. This is the key to the method of discussion employed throughout, but the writer's view is always presented in a manner sufficiently forceful to leave no room for misunderstanding.

At the outset, the importance of a knowledge of intermediate metabolism is explained, various sources of such information are critically discussed, and possible sources of error pointed out. There follows a consideration of ingenious theories of oxygen activation and, in the treatment of Traube's peroxide theory the reader is unconsciously prepared for the complicated matters which constitute the body of the book. Among the more important of these may be noted β-oxidation, the acetone substances, oxidation of side chains, alkaptonuria, tryptophane and the quinoline ring, lactic acid in its relation to carbohydrate metabolism, and the oxidation of purine derivatives.

But of especial interest is a chapter on the oxidation of α-amino acids in which the ground is taken that these substances give rise in the organism primarily to α-ketonic acids and not, as might have been supposed, to α-hydroxy acids. A number of matters are brought into harmony with this assumption. The ketonic acid is proposed as a connecting link between amino acids and carbohydrates and the argument culminates in a discussion of the experiment of Neubauer who

found that *d*-phenylacetic acid is converted by the dog's organism into *l*-mandelic acid—a result which seems to find its only explanation in ketonic acid formation.

The monograph is all that could be reasonably demanded of a text-book and more. It is fully up to the high standard of its companions in the Plimmer-Hopkins series.

WALTER JONES

DIE CHEMISCHE INDUSTRIE IN DEN VEREINIGTEN STAATEN UND DIE DEUTSCHEN HANDELSBEZIEHUNGEN. Auf Grund von amtlichem Material bearbeitet von DR. HERMANN GROSSMANN, Privatdozent an der Universität Berlin. Leipzig: Verlag von Veit & Co. 1912. pp. iv + 85. Price, M. 3.50.

This is a study of the chemical industries of the United States set forth for the benefit of the students of this subject in Germany and for that of the German manufacturer and merchandizer in the products of this industry. The author states that it is "auf Grund von amtlichem Material" and singularly, for a study presented by a privatdozent of the University of Berlin, very meager references are given to the sources from which the very considerable number of statistical tables which are presented have been compiled. The internal evidence shows that publications of the Bureaus of the Census and of Statistics and the Geological Survey have been made use of, but apparently in many instances secondary sources have been resorted to, though the original official publications are most freely at command and readily accessible. The chief reliance seems to have been placed on the Glossary of Schedule A published by the Tariff Board, which is a résumé of much of the official material contained in the above mentioned documents, but the tabular presentations made by the author do not usually coördinate with those of the last mentioned official document, or any of the others.

The subject is treated under the headings of "Die wirtschaftliche Entwicklungsgeschichte der nord-amerikanischen chemischen Industrie. Einfuhr und Ausfuhr von Chemikalien in der Gegenwart;" "Aus der wirtschaftlichen Entwicklungsgeschichte einzelner Zweige der amerikanischen chemischen Industrie;" "Der Handelsverkehr in Chemikalien zwischen Deutschland und den Vereinigten Staaten und die deutsche Handelsstatistik;" "Der neue Zolltarifentwurf für Chemikalien vom Jahre 1912;" "Anhang. Patente und chemische Industrie in den Vereinigten Staaten, von B. Herstein."

It is evident that the narrow view of the chemical industries which prevails in some quarters has controlled the mind of the author and that he has overlooked that broader view

which dominates in academic circles and which was set forth in the *Transactions of the American Institute of Chemical Engineers*.[1] He has, in consequence, overlooked that broader treatment of the patent relations which followed as a consequence of this more extended consideration of the realm of chemical technology.

The brochure is of interest as illustrating to American students the close relations existing in German universities between the investigator, the community, the state and the manufacturer, and as suggesting that there still exists in this country an unfulfilled duty of usefulness awaiting the university officer.

CHARLES E. MUNROE

ELEMENTARY APPLIED CHEMISTRY. By LEWIS B. ALLYN, Department of Chemistry, State Normal School, Westfield, Mass. Boston, New York, Chicago, London: Ginn & Co. pp. xi + 127.

This little book gives an extreme example of a tendency which is observed to too great an extent to-day in educational methods in this country. The revulsion of feeling from the former classical methods of education has produced a demand, even a mania, for things of direct practical value. That education is primarily for the development of the mind is a principle which seems to have fallen into disregard.

The reviewer rejoices with others that matters which have a direct bearing on the problems of life are coming to be recognized as a fit basis for intellectual training. The natural sciences develop the mind to fully as great activity and they give a broader view of life than do the ancient languages. But much of the unsystematic "Nature Study" of to-day, as well as chemistry from the vocational and informational standpoint, serves hardly more than to entertain the pupil; it adds little to his intellectual power, and the mere information, without the intellectual power to apply it to new problems, is of little value even in "practical life."

The book under consideration gives many tests, for the most part empirical, upon such materials as textile fabrics, soils, plants, foods, tooth powders, headache powders, wall papers, paints and oils, and urine. It devotes one section to procedures for dyeing raffia with natural and artificial colors, and another to the removal of stains. This book is only a laboratory guide and does not attempt to explain the chemistry of the materials examined. A few of the tests are for substances which could come within the comprehension of elementary students, and likewise a few of the reactions involved are of

[1] Vol. 2, 84-104 (1909).

a definite and sufficiently simple character to serve as a basis for the elementary study of chemistry. The mass of the material, however, is purely empirical, or its chemistry is far too complicated to be understood by beginners.

It is certain that this kind of laboratory work will arouse the interest and enthusiasm of a class of normal school students. Perhaps the author succeeds, with the impetus of this enthusiasm, in developing the scientific side of the subject in the classroom. These laboratory experiments, however, are not a suitable basis for an intelligent and logical study of the science of chemistry either in the laboratory or the classroom.

Assuming that for the purpose of arousing enthusiasm this sort of laboratory work is warranted, the book has much that is commendable. Considerable skill has been shown in compiling and adapting methods of testing foods and other products for students unpracticed in chemical manipulation; and some apparently original as well as ingenious and effective methods have been introduced. Too many inaccuracies and ambiguities in statements of facts and in directions are noted and these would frequently perplex a painstaking student.

Experts in food analysis often make mistakes, but they at least understand the complexity of their problem and realize when it is unsafe to give too much weight to their conclusions. It is difficult to see how an elementary pupil (not necessarily limiting the beginner to this class) can make of the course in question more than an attractive form of play, but there is some danger that the play may be taken in earnest and that the student may attain so much false confidence that harm may result from mistaken conclusions.

When all is said, there is no royal road to attainment, except that which involves diligent, and at times uninteresting, plodding. Nevertheless, pupils and sometimes even teachers become filled with the pride of accomplishment if they can jump at once to the attack of important problems and delude themselves that they are accomplishing something while others more methodical would still be laboring to prepare themselves in the rudiments.

In conclusion, the reviewer offers the opinion that, although it is most commendable to add interest to the study of chemistry through its applications to practical problems, it is essential to start with simple substances within the comprehension of the student, and that it is a mistake, even in a brief course, to venture deeper into involved practical matters than the student's understanding will warrant. ARTHUR A. BLANCHARD

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume V. Tannins, Analysis of Leather, Dyes and Colouring Matters, Dyestuffs of Groups 6 to 12, Colouring Matters of Natural Origin, Analysis of Colouring Matters, Colouring Matters in Foods, Inks. By the Editors and the following contributors: W. P. DREAPER, J. F. HEWITT, W. M. GARDNER, ALBERT F. SEEKER, PERCY H. WALKER, E. FEILMANN. Fourth Edition. Entirely Rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., Formerly Lecturer and Assistant in the Chemical Research Laboratory, City and Guilds College, Imperial College of Science and Technology, London, and SAMUEL S. SADTLER, S.B. Philadelphia: P. Blakiston's Son & Co. 1911. pp. IX + 704. Price, $5.00.

The text of the present volume has been prepared by six contributors, each of established reputation in his chosen topic. Developments in the field covered since the issue of the preceding edition have made necessary many additions and changes in the subject matter. These have on the whole been very judiciously effected without radically altering the general arrangement.

The chapters on tannins and their analysis, and on the analysis of leather are furnished by W. P. Dreaper, and include in their new matter the standard American and European "official" methods. The general description of the properties, reactions, classifications, and uses of the dyestuffs occupies 320 pages, or nearly half the reading matter of the volume. The section on nitro, nitroso, azoxy, pyrazolone, azo, and hydroxyketone colors is the work of W. P. Dreaper and E. Feilmann. The synthetic colors belonging to other classes are treated by J. F. Hewitt, while M. W. Gardner describes the colors of natural origin. The chemical examination of coloring materials in substance, on fibers, or in lakes, is treated in 186 pages by Messrs. Dreaper and Feilmann, Green's most recent procedures, supplemented by tables giving the color reactions of the dyed fibers with acids, alkalies and stannous chloride, being given in full. The chapter of 45 pages by A. F. Seeker on coloring matters in foods is an entirely new section of the book which adds materially to its value. The final chapter, by P. H. Walker, deals with the examination of inks, ink marks, typewriter ribbons, and carbon papers.

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